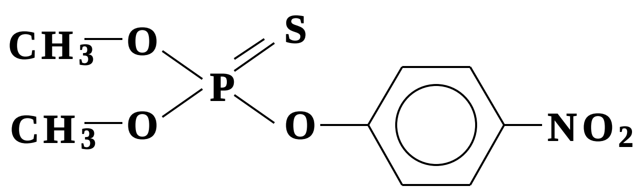
EVALUATION OF METHYL PARATHION AS A TOXIC AIR CONTAMINANT



Part A

Environmental Fate

California Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch

California Environmental Protection Agency
Sacramento, California

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Department of Pesticide Regulation

Paul E. Helliker
Director

For additional copies of this report please contact:

Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch
830 K Street
Sacramento, California 95814-3510

(916) 324-4100

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DISCLAIMER

The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

TABLE OF CONTENTS

List of Tables

List of Figures.

THE EVALUATION OF METHYL PARATHION AS A TOXIC AIR CONTAMINANT

PART A—THE ENVIRONMENTAL FATE OF METHYL PARATHION

1. INTRODUCTION

Assembly Bills 1807 and 3219 establish the criteria necessary for the identification and control of toxic air contaminants (TACs) in California. These laws mandate the Director of the Department of Pesticide Regulation (DPR) to determine which pesticides may qualify as TACs (Food and Agricultural Code, § 14021 *et seq.*). The Food and Agricultural Code (FAC) defines TACs as air pollutants that may cause or contribute to an increase in mortality or an increase in serious illness, or that may pose a present or potential hazard to human health (FAC, § 14023[d]). AB 3219 sets specific timelines for the investigation and review of registered pesticides as possible TACs, requires public hearings in the TAC determination process, and enacts civil penalties for non-compliance of permit, use and mitigation conditions established by DPR.

Once a pesticide has been identified as a TAC, DPR is required to determine, in consultation with the Office of Environmental Health Hazard Assessment (OEHHA), the Air Resources Board (ARB), and with the air pollution control districts and air quality management districts of the affected counties, the need for, and appropriate degree of, control measures (§ 14024 et seq., FAC). As part of the identification process, the law mandates the preparation of a health effects document (HED) that assesses the health effects and estimates levels of exposure for each candidate pesticide (FAC, § 14023). DRP prepares the HED, which is subsequently reviewed by the Air Resources Board (ARB), Office of Environmental Health Hazard Assessment (OEHHA), Department of Health Services, the Scientific Review Panel (SRP), the pesticide registrants and the public. Following review and acceptance by the SRP, the HED forms the basis for the Director's determination whether the pesticide is a TAC.

The HED consists of three parts: 1) Part A—Environmental Fate; 2) Part B—Public Exposure Assessment; and 3) Part C—Risk Characterization. Part A consists of a review of: (a) the scientific literature concerning the environmental fate, and the physical and chemical characteristics of methyl parathion; (b) application, patterns of use, and formulations specific to California; and (c) the results of two California air monitoring studies conducted by ARB staff to monitor the concentration of methyl parathion and it's breakdown product—methyl paraoxon—in air. Monitoring was performed in several communities in Colusa and Sutter Counties over a six week period corresponding with seasonal applications to flooded rice fields. Part B, the exposure assessment, contains estimates of human exposure to airborne concentrations of methyl parathion and methyl paraoxon. Part C reviews the health effects, and includes: (a) an assessment of the availability and the quality of data on health effects, and (b) the range of risk to humans resulting from the current or anticipated exposure to methyl parathion and methyl paraoxon in air where there is a threshold of significant adverse health effects.

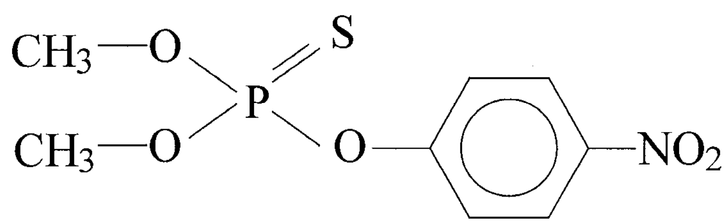
Methyl parathion entered the AB 1807/3219 process in 1984 when it was added to DPR's *Plan for the Implementation of Assembly Bills 1807 and 3219* (Langley, 1987). Methyl parathion was also listed as a candidate for evaluation in DPR's *Modifications and Additions to the Candidate Toxic Air Contaminant List* (Oudiz et al. 1989) and the report *Pesticides for Evaluation as Candidate Toxic Air Contaminants* (Kelley and Reed, 1996). This report contains background and use information regarding the pesticide methyl parathion. DPR has included information on methyl paraoxon in this HED because it is the toxicologically significant breakdown product of methyl parathion in the environment.

1.1. Methyl Parathion as a Chemical Compound

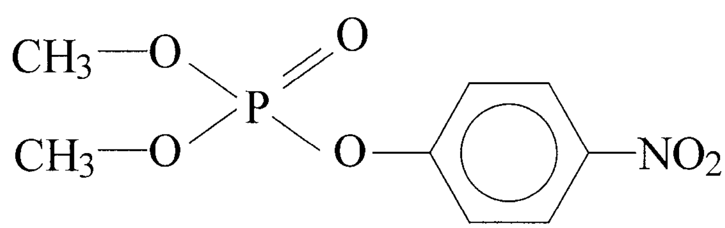
Methyl parathion [Chemical Abstracts Service (CAS) Registry Number 298-00-0] (Royal Society, 1993) is known by a variety of synonyms among which include azophos, metaphos (Russia), methylthiophos, oleovofotox, parathion-methyl, paratox (India), vofatox and wofatos (Lewis, 1991). Methyl parathion's structure is shown below (Figure 1a). In the environment, methyl parathion rapidly oxidizes to the more toxic oxon analogue, methyl paraoxon, shown in Figure 1b (Royal Society, 1993). This conversion requires the substitution of oxygen for sulfur on the phosphorus atom.

FIGURE 1. The Chemical Structures of Methyl Parathion and Methyl Paraoxon.

a) Methyl Parathion



b) Methyl Paraoxon



1.2. Toxicity and the Regulation of Methyl Parathion

The acute oral toxicity of methyl parathion in rats ranges from an LD_{50} of 2.9 mg/kg (WHO, 1984) to an LD_{50} of 24.5 mg/kg (Miamoto *et al.*, 1963). This toxicity is similar to that of ethyl parathion (LD_{50} values range from 2.0 to 30.0 mg/kg) (EPA, 1975). Dermal LD_{50} values of methyl and ethyl parathion in rats have been reported to be as low as 63 mg/kg (NIOSH, 1987) and 6.8 mg/kg (NIOSH, 1976), respectively.

DPR regulates certain pesticides as "Restricted Materials" based on criteria listed in the Food and Agricultural Code (§ 14004.5). These materials may be hazardous to public health, farm workers, domestic animals, wildlife, the environment, or to other crop plants. Methyl parathion is a restricted material because it is classified as a Category I (highly toxic) pesticide. It is classified as such because methyl parathion possesses an oral LD_{50} less than 50 mg/kg, one requirement for Category I classification (Title 40, Code of Federal Regulations, § 156.10).

Due to methyl parathion's acute toxicity, and in order to prevent methyl parathion-related illnesses and injuries in agricultural workers, DPR adopted regulations to ensure worker safety during handling and application of methyl parathion. Label instructions require that workers involved in the mixing and loading operations must wear protective clothing, including face shield and respirator, and that these operations must be accomplished by using a closed mixing system.

Other regulations have been adopted by the State of California governing the length of time that must pass between application and the re-entry of fields by farm workers. Workers may re-enter fields treated with methyl parathion two days following an application if the application rate was 1 lb. active ingredient (AI)/acre or less, or if a micro-encapsulated formulation was used. Re-entry intervals of 14 days have been adopted when methyl parathion is applied to apples, citrus, corn, or grapes specifically, and for all other crops when application rates exceed 1 lb. AI/acre. Irrespective of formulation or amount applied, re-entry intervals are 21 days for peaches and nectarines.

As a result of the implementation of these regulations, reported illnesses and injuries attributable to methyl parathion remain low in California. Each year, the Worker Health and Safety Branch of DPR produces the "Annual Summary of Pesticide Related Illnesses and Injuries." A review of these summaries for the thirteen-year period 1982 through 1994, shows that methyl parathion was the causative agent in seven inadvertent poisoning episodes (CDPR 1996, 1995, 1994, 1994, 1993, 1991, 1990: CDFA 1988, 1987, 1986, 1985, 1984, 1983). Poisoning episodes occurred as follows: in 1982, two systemic illnesses and one eye injury; in 1983, one systemic illness (due to an application by hand); in 1984, one dermal injury (due to field residue); in 1985, no illness/injury; in 1986, no illness/injury; in 1987 one systemic illness; in 1988, no illness/injury; in 1989, no illness/injury; in 1990, no illness/injury; in 1991, one possible systemic illness; in 1992, no illness/injury; in 1993, no illness/injury; and in 1994, no illness/injury. These data indicate that despite the potential toxicity of methyl parathion, the incidence of illness/injury associated with its use remains low.

Part A---Environmental Fate

Historically, methyl parathion has been widely used in California. Methyl parathion has a short residual life, is relatively inexpensive to use, and has broad-spectrum activity against a variety of agricultural pests. However, methyl parathion's broad spectrum, non-selective mode of action places it at a disadvantage when compared with the newer, less toxic, more selective pesticides now available. Additionally, Wolfenbarger *et al.* (1984) have demonstrated the development of resistance to methyl parathion in some insect species.

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2. PROPERTIES OF METHYL PARATHION

The following sections summarize the physical and chemical properties of methyl parathion and methyl paraoxon.

2.1. Physical and Chemical Properties of Methyl Parathion and Methyl Paraoxon

Methyl parathion (CAS: 298-00-0) has the molecular formula $C_8H_{10}NO_5PS$, and a molecular weight of 263.21 AU. At room temperature methyl parathion is in the form of colorless crystals which emit a faint garlic-like odor. Methyl parathion melts at 35-36 °C, and has a boiling point of 154 °C at 136 Pa (Tomlin 1994). Methyl parathion is sparingly soluble in water 55 to 60 mg/L at 25 °C. It is slightly soluble in petroleum distillates and readily soluble in most organic solvents. Table 1 summarizes the physical and chemical properties of methyl parathion.

Methyl paraoxon (CAS: 950-35-6) has the molecular formula $C_8H_{10}NO_5PO$ and a molecular weight of 247.14. As a breakdown product of methyl parathion, it is of toxicological interest. There is no information regarding the physical or chemical properties of methyl paraoxon.

Methyl parathion (O,O-dimethyl O-4-nitrophenyl phosphorothioate) has chemical properties and a mode of action similar to those of ethyl parathion, but methyl parathion isomerizes more readily and hydrolyzes four to five times more rapidly than ethyl parathion (Spencer, 1968; The Royal Society of Chemistry, 1983, 1991). For these reasons, methyl parathion is less persistent as a residue on foliage or in soil, and it is less stable in storage than ethyl parathion. Chemical and physical properties of methyl parathion which relate to its presence and persistence in air as well as a representative sample of currently active formulations and product names (May, 1999) are presented in Table 1.

The most common breakdown product of methyl parathion is p-Nitrophenol, produced through either of two environmental processes (Figure 2). The first process involves the hydrolysis of methyl parathion to p-nitrophenol and dimethyl phosphorothioic acid. The second process involves the oxidation of methyl parathion to methyl paraoxon and a further subsequent hydrolysis of methyl paraoxon to p-nitrophenol and dimethyl phosphoric acid.

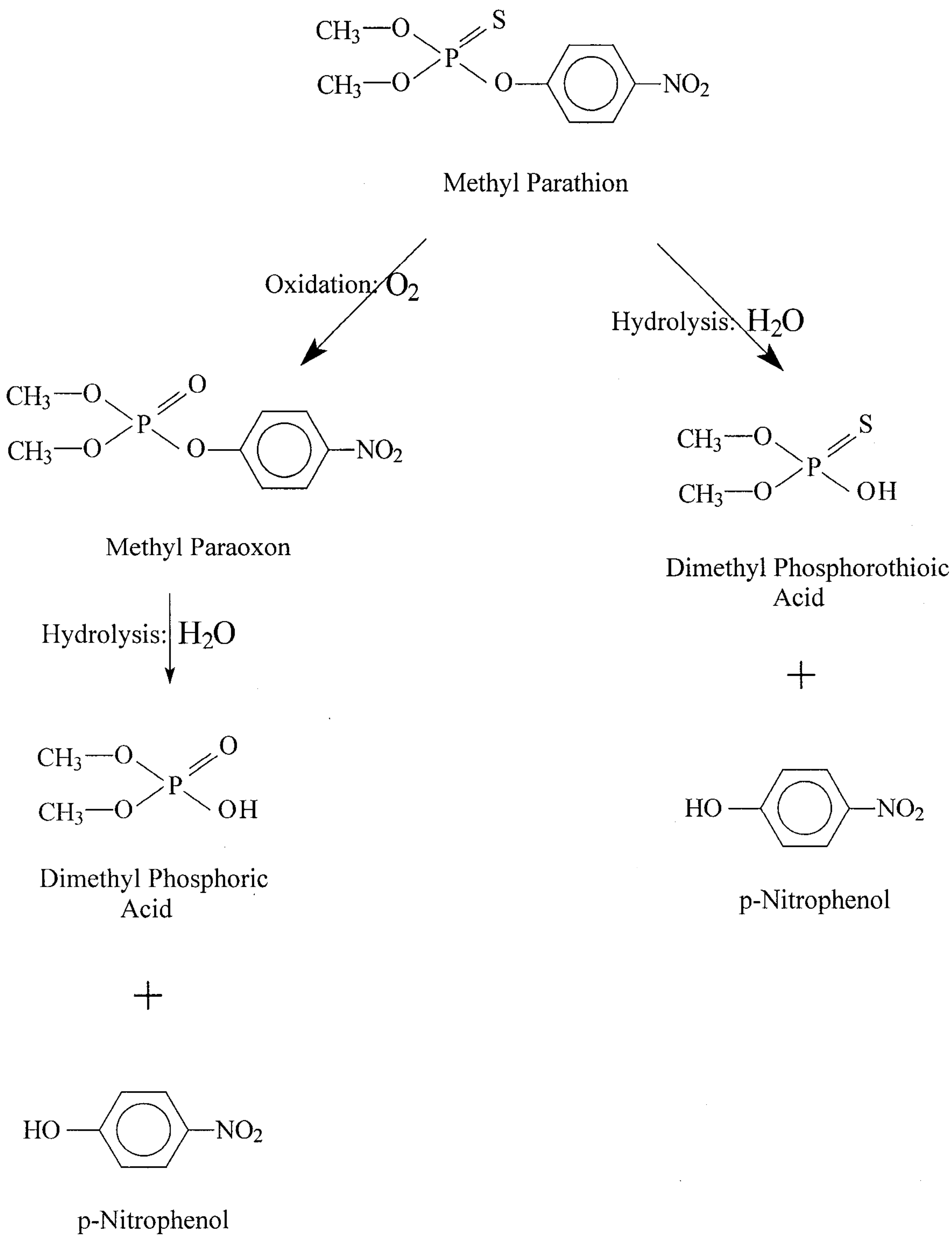
TABLE 1. Characteristics of Methyl Parathion[a]

CATEGORY	PROPERTY
Chemical Names:	O,O-dimethyl O-4-nitrophenyl phosphorothioate O,O-dimethyl O-(4-nitrophenyl) thiophosphate
Other Names:	metaphos (Russia), paratox (India)
Formulation Types:	Emulsifiable concentrate, microencapsulated formulation.
Some Trade Names:	Helena 4 lb. Methyl Parathion, Pencap-M Microencapsulated Insecticide, Wilbur-Ellis Methyl Parathion 5 Spray
CAS Registry Number:	298-00-0
Molecular Formula:	$C_8H_{10}NO_5PS$
Molecular Weight:	263.21
Physical Form:	Colorless crystals
Melting Point:	35–36 °C
Boiling Point:	119 °C at 0.13 mbar 154 °C at 1.3 mbar
Vapor Pressure:	1.3 mPa at 20 °C[b] 2.3 mPa at 25 °C[c] 5.3 mPa at 30 °C[c]
Solubility:	55 to 60 mg/l in water at 25 °C, Slightly soluble in petroleum distillates. Readily soluble in organic solvents.
Henry's Law Constant:	10.3×10^{-8} atmomole/m^3[d]
Specific Gravity (25/4 °C):	1.265
Stability:	Hydrolyzed in alkaline and acidic media approximately five times more rapidly than ethyl parathion. Isomerizes upon heating.
Conversion Factors[e]:	1 ng/m^3 = 0.099 ppt 1 ppt = 10.1 ng/m^3

[a]/ From The Royal Society of Chemistry, 1993, except as indicated.
[b]/ Guckel *et al.*, 1973.
[c]/ Spencer *et al.*, 1968.
[d]/ Seiber and McChesney, 1987
[e]/ See Appendix 1 for equation.

FIGURE 2.

Environmental Fate of Methyl Parathion



2.2. Synonyms

The following is a list of synonyms for methyl parathion. Synonyms are common names, chemical names and the more common trade names. Methyl parathion names used in this document are in bold type (The Royal Society of Chemistry, 1983, 1993; Montgomery, 1993; Lewis, 1991.)

A-GRO * AZOFOS * AZOPHOS * BAY E-601 * BAY 11405 * BLADAN-M * CEKUMETHION * DALF * DEVITHION * O,O-DIMETHYL-O-pNITROPHENYLESTER KYSELINY THIOFOSFORECNE (CZECH) * O,O-DIMETHYL-O-(4-NITROFENYL)-MONOTHIOFOSFAAT (DUTCH) * DIMETHYL p-NITROPHENYL MONOTHIOPHOSPHATE * O,O,-DIMETHYL-O-(4-NITRO-PHENYL)-MONOTHIOPHOSPHAT (GERMAN) * O,O,-DIMETHYL-O-(p-NITROPHENYL) PHOSPHOROTHIOATE * **O,O-DIMETHYL O-4-NITROPHENYL PHOSPHOROTHIOATE** * O,O,-DIMETHYL-O-(4-NITROPHENYL)-PHOSPHOROTHIOATE * DIMETHYL 4-NITROPHENYLPHOSPHOROTHIOATE. * O,O,-DIMETHYL-O-(p-NITROPHENYL)-THIONOPHOSPHAT (GERMAN) * O,O,-DIMETHYL-O-(4-NITROPHENYL)-THIONOPHOSPHAT (GERMAN) * DIMETHYL-p-NITROPHENYL THIONPHOSPHATE * DIMETHYL p-NITROPHENYL THIONPHOSPHATE. * O,O-DIMETHYL-O-p-NITROPHENYL THIOPHOSPHATE * DIMETHYL PARATHION * O,O-DIMETHYL-O-(4-NITRO-FENIL)MONOFOSFATO (ITALIAN) * DREXEL METHEL PARATHION 4E * ENT 17,292 * FOLIDOL M * GEARPHOS * ME-PARATHION * MEPATON * MEPTOX * METACIDE * METAFOS * METAPHOR * METAPHOS * METHYL-E 605 * METHYL FOSFERNO * METHYL NIRAN * **METHYL PARATHION** * METHYLTHIOPHOS * METILPARATHION (HUNGARIAN) * METRON * METYLOPARATHION (POLISH) * METYLPARATHION (CZECH) * NCI-C02971 * p-NITROPHENYLDIMETHYLTHIONOPHOSPHATE * NITROX * OLEOVOFOTOX * PARAPEST M50 * PARATAF * M-PARATHION * OARATHION METHYL * PARATHION-METILE (ITALIAN) * PARATOX * PENCAP-M * PHOSPHOROTHIOIC ACID O,O-DIMETHYL O-(p-NITROPHENYL) ESTER * RCRA WASTE NUMBER PO71 * SINAFID M-48 * SIXTY-THREE SPECIAL E.C. INSECTICIDE * TEKWASIA * THIOPHENIT * THIOPHSPHARE DE O,O-DIMETHYL ET DE O-(4-NITROPHENYLE) (FRENCH) * THYLFAR M-50 * TOLL * VERTAC METHYL PARATHION TECHNISCH 80% * VOFATOX * WOFATOS * WOFATOX * WOFOTOX *

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3. APPLICATION, USE PATTERNS, AND FORMULATIONS OF METHYL PARATHION

This chapter includes information concerning the use, methods of application, the range of amounts applied, and a description of the formulations of methyl parathion currently available. The use of all pesticides is indexed yearly in the Annual Pesticide Use Report, which is available in printed form in two volumes. The first volume is indexed by chemical, and lists each crop or commodity the pesticide was used on that year. The second volume is indexed by crop or commodity, and lists all pesticides applied thereon that year. DPR also makes available the raw data on which these reports are based. For the purposes of this report, all use information (from 1990 through 1998) was obtained from the raw data. Use information before 1990 was obtained from DPR's printed Use Reports.

3.1. Methyl Parathion Formulations

Five methyl parathion–containing products remain registered (May, 1999) for use in California. Variations in methyl parathion formulations have been developed to address two concerns: 1) to decrease volatility and increase its half-life on foliage; and 2) to decrease its toxicity to non-target organisms by reducing potential exposure. Formulations of methyl parathion that are currently registered in California include: four–emulsifiable concentrates, and one–microencapsulated product. Of the four- emulsifiable concentrates, one is admixed with the pesticide thiodan. The microencapsulated form works as a stomach poison following ingestion by gnawing and chewing insects. Emulsifiable concentrate formulations work as both contact and stomach poisons.

When encapsulated, methyl parathion is less volatile. Lower volatility should lead to a slower accumulation of methyl parathion in the atmosphere, and increased persistence on foliar and soil surfaces. Cardarelli (1976) reported that the period of effective pest control for two methyl parathion formulations, applied at identical rates, was 5 to 8 days for the encapsulated formulation, but only 1 to 3 days for the emulsifiable concentrate. Smith *et al.* (1987) reported a half-life of 28 hours for the encapsulated formulation compared with 4.4 hours for the emulsifiable concentrate. Jackson and Lewis (1978; 1979) measured methyl parathion in the air near treated fields and found that the use of the encapsulated formulation resulted in lower atmospheric levels when compared with air concentrations occurring after application of an emulsifiable formulation. In contrast, Pass and Dorough (1973) found that the dissipation rates for both the microencapsulated and the emulsifiable formulations were rapid, with more than 90 percent of total detectable residues dissipating within three days of application.

3.2. Timing of Application, Methods of Application, and Recommended Label Rates

3.2.1. Timing of Application

Methyl parathion is an insecticide-acaricide, used to control insect and other invertebrate pests of crops. It is used to control lepidopterous pests (armyworm, alfalfa caterpillar, apple pandemis, western yellow-striped armyworm, orange tortrix) on alfalfa, almond, apricot, peach, and other stone fruits, small grains, peppers, sugarbeets and tomatoes. Methyl parathion is used extensively in rice cultivation for the control of the rice leafminer, and the tadpole shrimp. Methyl parathion is also used for the control of aphids, grasshoppers, leafminers, scale, spider mites, and other pests, and for the control of mosquitoes in irrigated pastures. Methyl parathion is currently registered and used on over 35 agricultural crops, in and around nurseries and nursery plantings, for public health control, regulatory pest control and landscape maintenance.

Because of its relatively short residual life, methyl parathion is often applied on an as-needed basis for the control of pests. Methyl parathion is generally applied following the first signs of pest damage. In many instances, sampling the pest populations is recommended before initiating control measures. For most commodities, methyl parathion has a re-entry interval of 48 hours following application and a post-harvest interval (time from final application to harvest) ranging from 5 (potato) to 21 days (beans, lettuce, stone fruits). The pre-harvest intervals are greater for commodities where the harvested plant part was directly treated.

3.2.2. Methods of Application

Depending on crop type and season of application, restrictions on application method and timing-of-application may be in effect. Methyl parathion has a well-known toxicity to honeybees, and its use is contraindicated when bees are visiting fields. Labels suggest that methyl parathion not be applied in almonds, alfalfa, and to fields where other crops or weeds are in bloom. This is especially true for the microencapsulated formulation. Methyl parathion may be applied with ground-based equipment, or via rotary or fixed-winged aircraft depending on commodity, season, and soil conditions. In 1988, approximately 85% of methyl parathion applications occurred by aircraft. For example, methyl parathion is applied aerially to flooded rice fields, via ground-blast spray equipment in orchard environments, and ground based spray equipment in a variety of other crop situations. Label language specifically prohibits applications made via chemigation.

When added to tank mixes containing methyl parathion, certain substances increase methyl parathion's persistence in the field following application. Buck *et al.* (1980), showed that the addition of the insecticide toxaphene (no longer registered for use in California) increased the persistence of methyl parathion on foliar surfaces. These authors proposed two mechanisms by which toxaphene may increase methyl parathion's persistence. It may act: 1) as an ultraviolet sunscreen, inhibiting the photo-oxidation of methyl parathion to methyl paraoxon; or 2) as a protective film to physically decrease methyl parathion's volatility from foliar surfaces. Ware *et al.* (1980) showed that toxaphene may also prevent the actual dislodging of methyl parathion from plant surfaces by rainfall or sprinkler irrigation. Similarly, molasses or oil was found to extend the residual life of methyl parathion when they were added to tank mixes (Ware *et al.*, 1980; Cole *et al.*, 1986). Although these authors offer no mechanism by which methyl parathion's residual life was extended, it is possible that these additives prevent methyl parathion's hydrolyzation. Addition of methyl parathion to highly alkaline materials such as lime or lime-sulfur solutions is not recommended. Clark *et al.* (1987) showed that pesticides admixed with alkaline compounds, such as calcium chloride, experienced enhanced degradation and reduced effectiveness. For methyl parathion, alkaline solutions enhance hydrolytic reactions in the tank mixture (see Figure 2).

3.2.3. Recommended Label Rates

In general agricultural applications, methyl parathion application rates range from 0.25 lb AI/acre to 3.0 lbs AI/acre, depending on target pest, season of application, and part of plant treated vs. part harvested. For leafy vegetables, small grains, and other vegetable applications, methyl parathion is applied at rates from 0.25 lb AI/acre to 1.0 lbs AI/acre. For stone fruits, grapes, and nut crops, methyl parathion may be applied from one to three lbs AI/acre. Application rates as low as 0.0625 lb AI/acre is recommended for low volume sprays for mosquito control in irrigated pastures. Finally, recommended label rates for the micro-encapsulated formulation range from 0.125 lb AI/acre to 3.0 lbs AI/acre.

3.3. Application of Methyl Parathion in California

3.3.1. Historical Use from 1977 to 1995

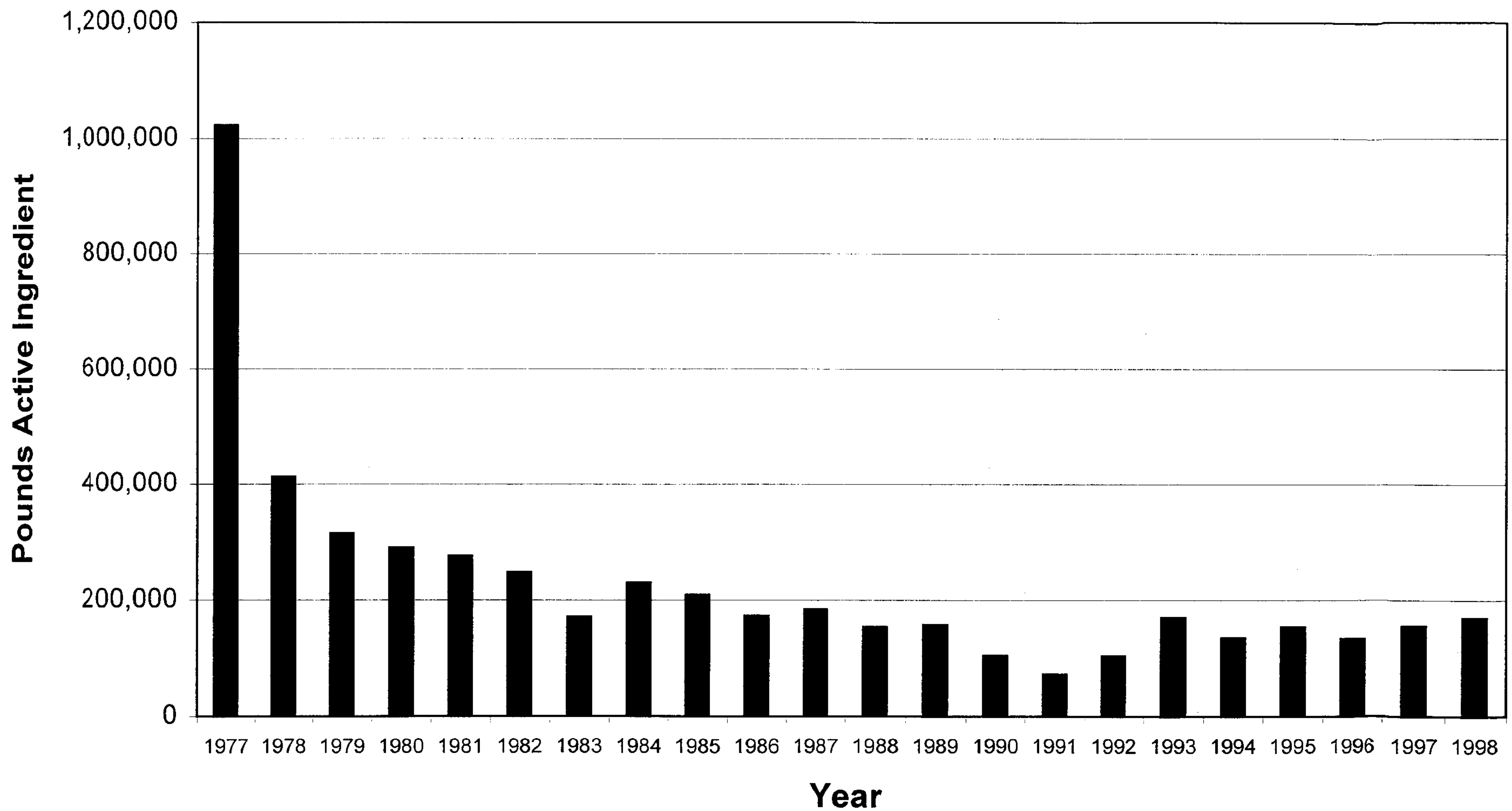
The amount of methyl parathion applied yearly in California has declined since the mid 1970's (Table 2). The amount of methyl parathion applied in California from 1977 through 1998 is shown in Figure 3. Since few of the pesticide use reports published before 1977 are still currently available, the full scope of methyl parathion's use before 1977 remains unclear. However, for the years before 1977 where use information is still available, more that 1.2 million pounds of methyl parathion AI had been applied each year.

TABLE 2. Historical Use of Methyl Parathion in California 1977 – 1995 (Pounds Active Ingredient)

YEAR	POUNDS AI	YEAR	POUNDS AI
1977	1,022,648	1988	153,457
1978	412,432	1989	157,129
1979	314,748	1990	104,977
1980	289,795	1991	72,510
1981	275,959	1992	103,457
1982	247,898	1993	169,542
1983	170,886	1994	135,128
1984	229,605	1995	153,557
1985	208,736	1996	133,419
1986	172,778	1997	155,023
1987	184,117	1998	168,909

In 1977, 1.02 million pounds of methyl parathion AI were applied in California. In 1978, use of methyl parathion decreased greatly when only 412,432 lbs AI were applied. Use again decreased in 1979, with 314,750 lbs AI used. Use of methyl parathion continued to decline throughout the 1980's, ranging from 290,000 lbs to 157,000 lbs. Average yearly use of methyl parathion for the decade of 1980 through 1989 was 209,000 lbs AI. In 1983, and from 1986 on, methyl parathion's yearly use has remained below 200,000 lbs AI. The decline in the use of methyl parathion has continued through the 1990's to the present time (1998). Average yearly use of methyl parathion for 1990 through 1998 was 132,950 lbs AI, ranging from a high of 169,542 lbs AI (1993) to a low of 72,510 lbs AI (1991).

Figure 3. Yearly Applications of Methyl Parathion in California (1977 - 1998)



3.3.2. Amounts Applied by County from 1990 - 1995

Figures for the historical use patterns for methyl parathion applications in California counties are presented in Table 3. In 1990, the greatest amounts of methyl parathion were applied to rice fields in Colusa, Sutter, Yuba, and Glenn counties. By 1998, high use had shifted to Contra Costa, Fresno, Lake, Sacramento, San Joaquin and Tulare Counties. Methyl parathion applications in Imperial County were relatively high in 1988 (25,500 lbs AI). Use dropped by almost 75 percent (to 5,650 lbs AI) by 1990, and use was almost eliminated by 1998 (127 lbs AI). Similar decreases in methyl parathion applications occur from 1991 through 1995 in Colusa, Glenn, Imperial, and Yuba counties. During this time methyl parathion use in Sutter County had almost doubled (Table 3).

In 1990, methyl parathion use in Fresno, San Joaquin, Sutter and Tulare Counties was relatively low, amounting to approximately twenty percent of use, 1,521 lbs AI, 5,356 lbs AI, and 2,279 lbs AI respectively (Table 3). Use increased in these three counties to 42 percent of all methyl parathion applied in 1992, to 51 percent in 1993, and to 56 percent in 1994. By 1995, methyl parathion's use in these counties increased to account for nearly sixty-five percent of the total amount applied; 33,681 lbs AI were applied in Fresno County, 15,425 lbs AI in San Joaquin County, 23,093 lbs AI in Sutter County, and 25,403 lbs AI in Tulare County. From 1996 through 1998, methyl parathion's use in these counties has hovered around fifth percent.

Methyl parathion applications exceeded 10,000 lbs AI during 1993 and 1995 in Kern County and during 1995 in Riverside County (Table 3). In the remaining Counties in California, methyl parathion's use fluctuates yearly yet use rarely exceeds 3,000 lbs AI/year. From 1990 through 1995, methyl parathion's use in these counties accounts for approximately thirteen to twenty-seven percent of yearly totals (22%, 1990; 27%, 1991; 20%, 1992; 20%, 1993; 13%, 1994; and 16%, 1995).

For the years 1995 through 1998, similar methyl parathion use patterns continued (Table 3). Use in Imperial County continued to decline, as did use in Colusa, Glenn, Kern, San Luis Obispo and Santa Cruz counties. Use of methyl parathion steadily increased in Contra Costa, Lake, Madera, Mendocino, Sacramento, San Joaquin and Tulare counties. Methyl parathion was applied sporadically in most other California counties during the 1990s.

TABLE 3. Methyl Parathion Use in California Counties and Their Respective Populations (1990-1995)[1].

COUNTY[2]	AMOUNT (LBS AI) METHYL PARATHION APPLIED									POPULATION
	1990	1991	1992	1993	1994	1995	1996	1997	1998	
Alameda	108	110	0	0	93	51	173	56	0	**1,279,182**
Butte	2,316	1,910	2,201	1,977	1,785	5,498	2,338	3,475	5,071	**182,120**
Colusa	27,137	7,114	12,110	13,979	7,768	4,013	3,949	2,729	1,036	**16,275**
Contra Costa	3,151	2,250	416	302	360	3,186	5,095	3,494	20,918	**803,732**
Fresno	1,521	6,212	17,055	32,912	26,641	33,681	22,453	20,577	21,764	**667,490**
Glenn	6,872	4,004	3,854	2,277	1,546	812	1,412	785	134	**24,798**
Imperial	5,653	4,665	3,173	3,052	2,009	1,061	702	407	127	**109,305**
Kern	2,771	1,732	7,521	10,630	5,365	10,310	702	407	127	**543,477**
Kings	0	1,140	1,462	3,842	2,631	1,013	1,893	4,237	2,173	**101,469**
Lake	0	0	0	40	91	1,435	2,661	4,538	11,966	**50,631**
Lassen	4,295	0	313	0	0	0	0	0	0	**27,598**
Los Angeles	0	1,478	651	343	839	106	28	26	84	**8,863,164**
Madera	0	348	986	4,300	7,370	3,591	3,550	2,831	1,512	**88,090**
Mendocino	0	0	0	45	0	1,005	1,065	1,710	2,602	**80,345**
Merced	585	1,298	523	120	1,342	462	195	3,799	866	**178,403**
Modoc	0	146	1,877	5,252	112	1,198	2,191	48	0	**9,678**
Monterey	1,300	3,246	659	90	78	166	95	104	97	**355,660**
Placer	0	1,248	1,874	9,096	847	487	781	617	342	**172,796**
Riverside	5,296	4,103	4,384	6,872	11,648	4,867	6,257	4,631	3,653	**1,170,413**

1/ From the 1990 US census.

2/ Counties are listed if the amount of methyl parathion applied active ingredient exceeds 50.0 lbs/year, or if the county was listed in Tables 5a, 5b, 5c, 5d, 5e, 5f, 5g, 5h, and/or 5i..

TABLE 3 con't. Methyl Parathion Use in California Counties and Their Respective Populations (1990-1995)[1].

COUNTY[2]	AMOUNT (LBS AI) METHYL PARATHION APPLIED									POPULATION
	1990	1991	1992	1993	1994	1995	1996	1997	1998	
Sacramento	1,635	1,228	1,622	2,058	1,102	1,956	8,598	5,717	15,230	**1,041,219**
San Benito	947	1,020	816	914	705	751	299	274	270	**36,697**
San Bernardino	524	192	153	84	73	289	1,152	0	37	**1,418,380**
San Joaquin	5,356	5,603	1,087	4,672	4,277	15,425	9,389	19,367	29,186	**480,628**
San Luis Obispo	1,462	284	2,263	1,409	255	1,183	193	256	0	**217,162**
Santa Barbara	574	488	747	325	220	277	213	0	2	**369,623**
Santa Clara	52	68	15	10	32	585	3	4	45	**1,497,577**
Santa Cruz	1,390	926	935	556	554	561	413	444	212	**229,734**
Siskiyou	0	199	1,614	4,257	2,028	652	624	101	0	**43,531**
Solano	31	300	0	0	1,622	1,340	2,153	2,202	2,053	**340,421**
Stanislaus	1,175	1,454	885	1,423	791	1,367	1,872	4,093	4,495	**370,522**
Sutter	14,394	10,787	12,753	23,889	15,102	23,093	16,885	15,055	5,875	**64,415**
Tulare	2,279	4,236	12,893	25,210	30,716	25,403	23,645	26,780	24,352	**311,921**
Ventura	447	235	842	270	400	198	0	206	205	**669,016**
Yolo	1,685	433	834	367	1,312	729	631	569	1,842	**141,092**
Yuba	8,816	3,653	6,627	7,909	4,954	6,667	9,579	7,914	4,886	**58,228**
Other	3,225	399	312	1,060	460	139	148	486	1,130	**7,754,386**
Totals	**104,997**	**72,509**	**103,457**	**169,542**	**135,128**	**153,557**	**133,419**	**155,032**	**168,909**	**29,769,178**

3.3.3. *Seasonal Application of Methyl Parathion from 1990 – 1995*

Methyl parathion applications in California follow a seasonal pattern (Figure 4). From 1990 through 1998, the greatest applications occur in May (52,159 lbs AI) followed by June (26,151 lbs AI), April (16,532 lbs AI), July (12,184 lbs AI), and March (7,435 lbs AI) (Table 4). Monthly use of methyl parathion, on a county-by-county basis, for the years 1990 through 1998 is presented in Tables 5a through 5i.

TABLE 4. Average Methyl Parathion Use by Month (1990 – 1998).

MONTH	AVERAGE USE	MONTH	AVERAGE USE
JANUARY	1,979	JULY	12,184
FEBRUARY	2,978	AUGUST	6,055
MARCH	7,435	SEPTEMBER	4,380
APRIL	16,532	OCTOBER	4,706
MAY	52,159	NOVEMBER	986
JUNE	26,151	DECEMBER	637

Originally, methyl parathion tended to peak in rice applications in Sutter, Colusa, Glenn Counties (Tables 5a-5c). However, in recent years, increased applications of methyl parathion to alfalfa, cotton, and stone fruit orchards has shifted the largest monthly applications to Fresno, San Joaquin and Sutter Counties (Tables 5d-5i).

3.3.4. *Amount applied to Crop Systems from 1990 - 1995*

As of October 1999, five methyl parathion–containing products are registered for use on over 35 crops grown agriculturally in California. These crops include: 1) field and forage crops – alfalfa, cotton, corn, small grains (barley, oats, wheat), grass, and legumes; 2) vegetable crops – beans, peas, peppers, potatoes, tomatoes; 3) leafy vegetables – lettuce, spinach, mustard greens or celery; 4) cole crops – broccoli, cabbage, cauliflower, or brussels sprouts, 5) stone fruits – apricots, cherries, almonds, peaches, nectarines, plums and prunes; and 6) pome fruits – apples, and pears. Methyl parathion may also be applied to non-agricultural lands and wetlands for mosquito control. Methyl parathion is no longer registered for use in nursery situations (ornamental flowers, shrubs, and trees), or for the control of insects in Christmas tree plantations and pine forests.

The amount of methyl parathion AI applied to commodities grown in California for the years 1990 through 1998 is summarized in Table 6. Methyl parathion applications to rice ranged from 51 percent of total use in 1990, to 20 percent by 1995, to 4% by 1998. Use on stone fruits rose from 8 percent in 1990, to 40 percent by 1995, and declined to 25% by 1998. Methyl Parathion use in grapes rose from 0.3 percent in 1990, to 14 percent by 1995, declining to 6% by 1998. Applications to pome fruits (apples and pears) rose from 2.4 percent to 37 percent during this time span. Finally, The amount of methyl parathion applied to alfalfa remained relatively constant through 1996, but has declined in 1997 and 1998. Use on beans and corn increased from 1996 on and use in walnuts rose from zero percent in 1990-1996 to 19% by 1998. For almost all other commodities, methyl parathion's use has decreased since 1990.

As an emulsifiable concentrate, methyl parathion is used on field and row crops (Table 6) and, historically, was often applied as a mixture with ethyl parathion. In Imperial County, growers historically applied methyl parathion to alfalfa in February and March, and to lettuce, cotton, and sugar beets in September and October. In Colusa County, methyl parathion is applied solely to rice, usually in May or early June. In other rice growing areas—Sutter, Glenn, and Butte Counties—methyl parathion is also applied during the May-June window. Chemigation (application through irrigation equipment) of methyl parathion is prohibited by U.S. EPA policy and application instructions on registered product labels.

In 1999, the U.S.EPA, severely curtailed the agricultural commodities to which methyl parathion may be applied. Applications to the following commodities have been eliminated: apples, carrots, certain beans and peas, cherries, grapes, nectarines, peaches, pears, plums, and tomatoes, and on other fruits and vegetables. Methyl parathion use will continue to be allowed on field-grown commodities; certain beans and peas, small grains (barley, oats, wheat) and rice. The total amount of methyl parathion applied, the seasonality and counties to which it is applied are all expected to change.

Figure 4. Seasonal Patterns of Methyl Parathion Application in California (Average use 1990 - 1998)

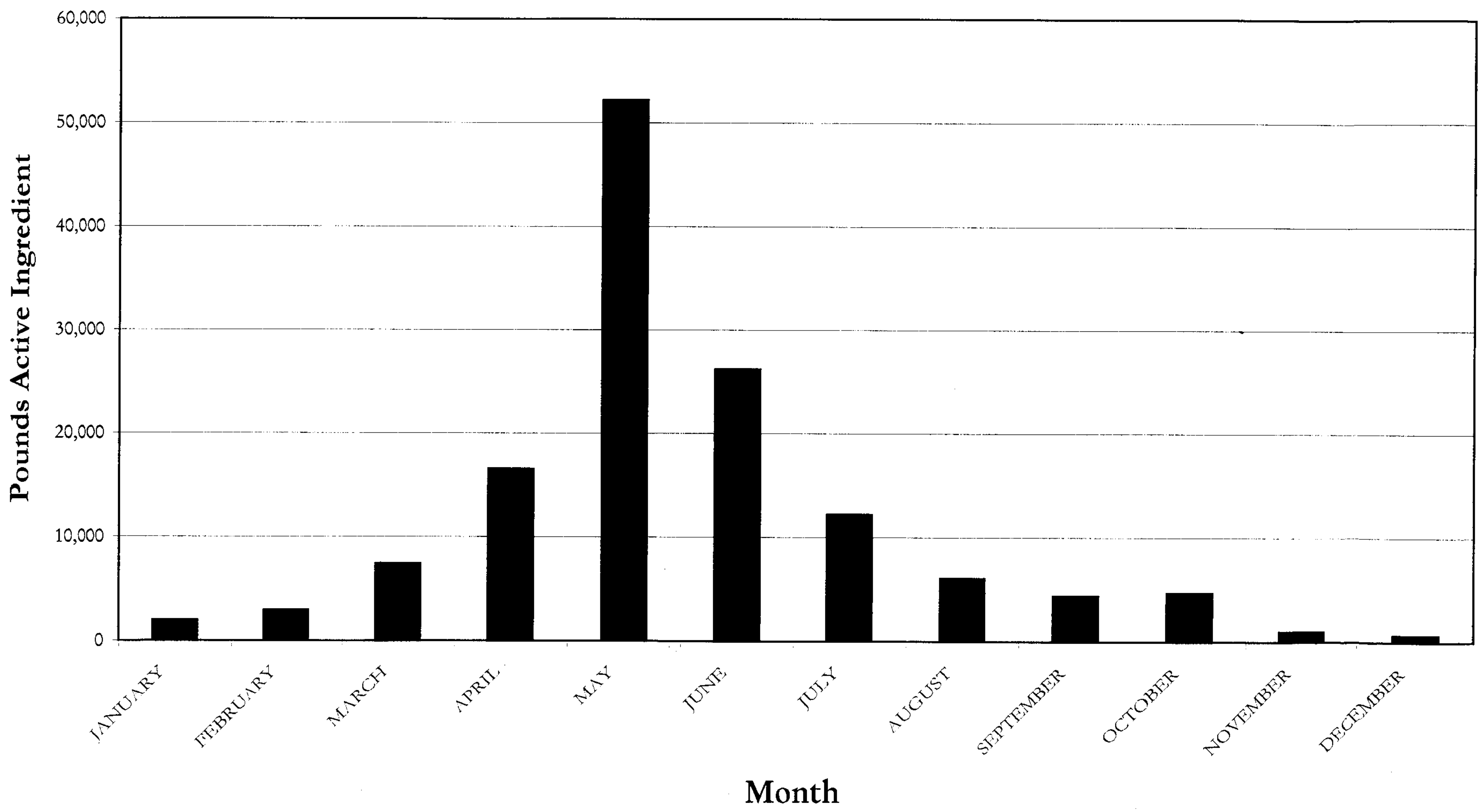


TABLE 5a: Monthly Applications of Methyl Parathion for 1990 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI	Feb.	lbs AI	March	lbs AI	April	lbs AI	May	lbs AI	June	lbs AI
Madera	264	Riverside	683	Butte	220	Butte	110	Butte	1,738	Butte	198
Stanislaus	133	SLO	726	CC	947	Colusa	1,165	Colusa	22,447	Colusa	1,220
Tulare	462	Sutter	132	Imperial	286	Kern	175	Fresno	572	CC	1,386
Yolo	267			Kern	193	Madera	132	Glenn	6,204	Glenn	683
				Monterey	751	Riverside	286	Lassen	441	Imperial	418
				Riverside	1,122	SJ	616	Placer	836	Placer	639
				SB	311	Stanislaus	109	Sac.	1,123	San Benito	509
				SJ	3,454	Tulare	309	Sutter	9,765	Santa Cruz	484
				SLO	616	Yuba	857	Tulare	682	Sutter	1,748
				SBo	418			Yuba	660	Yuba	1,213

July	lbs AI	Aug.	lbs AI	Sept.	lbs AI	Oct.	lbs AI	Nov.	lbs AI	Dec.	lbs AI
Colusa	352	Colusa	528	Imperial	902	Imperial	1,672	Imperial	418	Tulare	286
CC	665	Imperial	550	Kern	640	Kern	968	Riverside	133		
Fresno	329	Kings	110	Riverside	1,308	Riverside	373	Tulare	176		
Imperial	1386	Riverside	133	Sutter	396	Santa Cruz	1,319	Ventura	131		
Merced	421	SJ	440			Ventura	220				
San Benito	245	Siskiyou	376								
Santa Cruz	659	Stanislaus	154								
Stanislaus	374	Sutter	551								
Sutter	549	Yolo	242								
Yolo	462										

[1]/ County Abbreviatons: CC=Contra Costa; Sac=Sacramento ; SJ=San Joaquin; SBo=San Bernardino; SB= Santa Barbara; SLO= San Luis Obispo

TABLE 5b: Monthly Applications of Methyl Parathion for 1991 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI	Febr.	lbs AI	March	lbs AI	April	lbs AI	May	lbs AI	June	lbs AI
Monterey	1	Fresno	93	Alameda	110	Fresno	1,413	Butte	1,480	Butte	379
SJ	216	Imperial	185	CC	1,357	Kern	340	Fresno	1,358	Colusa	416
SLO	4	Merced	74	Fresno	107	Kings	383	Glenn	3,318	Fresno	1,549
SB	70	Monterey	67	Merced	189	Riverside	108	Kern	734	Glenn	686
Stanislaus	606	Orange	4	Riverside	1,731	San Benito	92	Placer	937	Los Angeles	1,149
Ventura	21	Riverside	1,015	SBo	72	SJ	432	Sac.	1,009	San Benito	381
		SB	28	SJ	3,009	SLO	77	SJ	895	SJ	571
		Tulare	122	SB	337	SB	61	Sutter	6,253	Sutter	2,589
				Solano	256	Stanislaus	238	Tulare	1,999	Tulare	424
				Sutter	226	Tulare	830	Yuba	1,359	Yuba	1,338

July	lbs AI	Aug.	lbs AI	Sept.	lbs AI	Oct.	lbs AI	Nov.	lbs AI	Dec.	lbs AI
Colusa	6,406	CC	73	Fresno	1,391	Imperial	2,070	Imperial	3	Riverside	2
Contra Costa	524	Imperial	660	Imperial	1,142	Kern	231	Monterey	71	San Benito	4
Fresno	280	Merced	399	Kern	302	Monterey	2,580	Riverside	54	San Mateo	1
Imperial	486	Riverside	291	Monterey	298	Riverside	322	San Benito	2	SB	1
Los Angeles	318	San Benito	99	Riverside	430	Santa Cruz	33	San Diego	2	Santa Clara	4
Merced	404	SJ	481	SB	13	Ventura	44	Santa Cruz	33	Stanislaus	135
San Benito	425	Stanislaus	182	Solano	44	Yolo	12	Tulare	185	Sutter	10
Santa Cruz	707	Sutter	423	Stanislaus	42			Ventura	63	Tulare	413
Sutter	1,248	Tulare	99	Sutter	5			Yolo	1	Ventura	63
Yuba	695	Yuba	241	Ventura	29					Yuba	6

[1]/ County Abbreviatons: CC = Contra Costa; Sac = Sacramento; SBo San Bernardino; SJ = San Joaquin; SB = Santa Barbara; SLO = San Luis Obispo

TABLE 5C: Monthly Applications of Methyl Parathion for 1992 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI	Feb.	lbs AI	March	lbs AI	April	lbs AI	May	lbs AI	June	lbs AI
Butte	96	Imperial	36	Fresno	483	Colusa	155	Butte	1,975	Colusa	966
Glenn	810	Monterey	75	Imperial	120	Fresno	3,767	Colusa	10,822	Fresno	4,122
Merced	456	Riverside	1,370	Kern	221	Kern	976	Fresno	5,772	Kern	1,375
San Benito	2	San Benito	3	Los Angeles	121	Kings	244	Glenn	2,326	Kings	444
Stanislaus	137	SB	112	Riverside	675	Los Angeles	175	Kern	1,777	Placer	485
Tulare	87	San Diego	1	SBo	29	Madera	149	Placer	1,390	San Benito	372
Ventura	80	SLO	14	SJ	413	Monterey	323	Sac.	1,358	SLO	658
		Stanislaus	12	SB	257	Riverside	785	Sutter	11,049	Sutter	1,384
		Tulare	56	Tulare	807	Tulare	4,988	Tulare	3,800	Tulare	1,398
		Ventura	59	Ventura	155	Yuba	872	Yuba	4,220	Yuba	892

July	lbs AI	Aug.	lbs AI	Sept.	lbs AI	Oct.	lbs AI	Nov.	lbs AI	Dec.	lbs AI
Fresno	1,362	Colusa	96	Colusa	35	Fresno	261	Imperial	98	Fresno	55
Kern	508	Fresno	946	Fresno	287	Imperial	1,583	Kern	75	Imperial	191
Modoc	1,446	Imperial	183	Glenn	488	Kern	73	Riverside	34	San Benito	8
SLO	1,315	Kern	188	Imperial	961	Riverside	135	San Benito	4	SLO	1
Santa Cruz	734	Modoc	403	Kern	2,327	San Benito	8	Santa Clara	2	SB	6
Siskiyou	987	San Benito	81	Riverside	376	Santa Clara	2	Tulare	386	Stanislaus	66
Stanislaus	381	SB	100	Sac.	29	Tulare	66	Ventura	12	Tulare	463
Sutter	246	Siskiyou	335	Santa Cruz	136	Ventura	169			Ventura	54
Tulare	418	Sutter	74	Tulare	230	Yolo	8				
Yuba	644	Tulare	194	Ventura	157						

1/ County Abbreviatons: Sac = Sacramento; SJ = San Joaquin; SBo San Bernardino; SJ San Joaquin, SB = Santa Barbara; SLO = San Luis Obispo

TABLE 5d: Monthly Applications of Methyl Parathion for 1993 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI	Feb.	lbs AI	March	lbs AI	April	lbs AI	May	lbs AI	June	lbs AI
Fresno	1,142	Fresno	108	CC	63	Fresno	6,049	Colusa	11,926	Butte	785
Riverside	570	Imperial	64	Fresno	274	Imperial	237	Fresno	12,386	Colusa	2,009
San Benito	4	Riverside	2,326	Imperial	242	Kern	1,522	Glenn	2,228	Fresno	4,191
Stanislaus	125	San Benito	4	Kern	319	Kings	128	Kings	2,641	Kern	1,502
Tulare	248	Santa Clara	0	Kings	232	Los Angeles	90	Madera	1,275	Madera	941
Yuba	105	Stanislaus	136	Los Angeles	248	Madera	1,774	Placer	4,955	Placer	4,141
		Tulare	125	Riverside	2,383	Riverside	457	Sac.	1,560	SLO	9476
		Ventura	55	SB	84	SB	242	Sutter	18,389	Sutter	4,277
				SJ	3,535	Tulare	6,859	Tulare	11,985	Tulare	1,449
				Tulare	292	Yuba	355	Yuba	4,803	Yuba	2,387

July	lbs AI	Aug.	lbs AI	Sept.	lbs AI	Oct.	lbs AI	Nov.	lbs AI	Dec.	lbs AI
Fresno	3,531	CC	91	Colusa	14	Fresno	1,121	Imperial	92	Fresno	479
Kern	1,220	Fresno	2,820	Fresno	812	Imperial	1,522	Kern	165	Imperial	69
Modoc	3,192	Kern	2,254	Imperial	826	Kern	1,592	San Benito	4	Santa Clara	1
Riverside	880	Kings	206	Kern	1,198	Madera	168	Santa Clara	1	Stanislaus	37
SLO	237	Modoc	2,060	Kings	5	San Benito	8	Tulare	39	Tulare	365
Santa Cruz	556	Riverside	254	Sac.	10	San Diego	3	Ventura	42	Ventura	53
Siskiyou	1,861	San Benito	227	San Benito	67	Santa Clara	3				
Sutter	1,120	Siskiyou	2,396	SLO	55	Tulare	626				
Tulare	2,142	Sutter	98	Tulare	442	Ventura	45				
Yuba	259	Tulare	638	Ventura	37	Yolo	6				

1/ County Abbreviatons: CC= Contra Costa; Sac = Sacramento; SJ = San Joaquin; SB = Santa Barbara; SLO = San Luis Obispo

TABLE 5e: Monthly Applications of Methyl Parathion for 1994 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI	Feb.	lbs AI	March	lbs AI	April	lbs AI	May	lbs AI	June	lbs AI
Fresno	2,941	Fresno	614	Alameda	42	Colusa	137	Butte	1,261	Butte	510
Kings	85	Los Angeles	19	Fresno	1,167	Fresno	7,034	Colusa	6,723	Colusa	909
Riverside	14	Madera	2,965	Kern	1,444	Kern	2,135	Fresno	8,781	Fresno	3,672
Santa Clara	1	Riverside	1,947	Los Angeles	438	Kings	830	Glenn	1,546	Madera	801
Tulare	1,230	San Benito	2	Madera	124	Madera	633	Kings	1,459	Sac.	258
Ventura	41	SB	19	Riverside	1,413	Riverside	1,446	Madera	1,896	San Benito	420
Yolo	700	Santa Clara	0	San Benito	54	Solano	252	Merced	1,305	Solano	859
		Tulare	387	SJ	2,659	Sutter	397	Sutter	11,399	Sutter	3,135
		Ventura	75	SB	186	Tulare	7,589	Tulare	11,909	Tulare	4,934
				Tulare	2,749	Yuba	903	Yuba	3,165	Yuba	884

July	lbs AI	Aug.	lbs AI	Sept.	lbs AI	Oct.	lbs AI	Nov.	lbs AI	Dec.	lbs AI
Contra Costa	74	Alameda	51	Fresno	71	Contra Costa	24	Fresno	102	Fresno	113
Fresno	1,250	Contra Costa	79	Imperial	669	Fresno	562	Imperial	35	Madera	560
Kern	123	Fresno	335	Kern	73	Imperial	1,305	Riverside	2,519	Riverside	162
Los Angeles	123	Kern	233	Kings	22	Kern	177	San Benito	4	San Benito	7
Riverside	130	Los Angeles	179	Sac.	560	San Benito	9	Santa Clara	3	Santa Clara	1
SJ	930	Madera	336	San Benito	22	Santa Clara	3	Ventura	45	Stanislaus	143
Santa Cruz	327	SJ	170	Stanislaus	14	Tulare	139	Yolo	3	Tulare	306
Siskiyou	1,894	Siskiyou	133	Tulare	470	Ventura	122			Ventura	45
Stanislaus	125	Sutter	132	Ventura	46	Yolo	19				
Tulare	755	Tulare	249	Yolo	19						

[1]/ County Abbreviatons: Sac = Sacramento; SJ = San Joaquin; SB = Santa Barbara; SLO = San Luis Obispo

TABLE 5f: Monthly Applications of Methyl Parathion for 1995 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI	Feb.	lbs AI	March	lbs AI	April	lbs AI	May	lbs AI	June	lbs AI
Butte	1,080	Colusa	48	Contra Costa	982	Fresno	11,308	Colusa	3,168	Butte	3,923
Fresno	1,594	Fresno	401	Fresno	3,467	Imperial	78	Fresno	10,084	Fresno	2,821
Imperial	57	Imperial	252	Imperial	86	Kern	2,248	Kern	2,622	Kern	2,832
Riverside	16	Kern	29	Kern	37	Kings	101	Madera	1,556	Sac.	945
San Benito	4	Riverside	2,156	Los Angeles	106	Riverside	824	Mendocino	844	SJ	2,908
Tulare	231	SB	73	Madera	224	SJ	3,483	Sac.	971	Solano	977
Ventura	19	Santa Clara	580	Riverside	1,363	SLO	1,019	SJ	1,810	Stanislaus	1,108
		Stanislaus	87	SJ	5,176	Sutter	45	Sutter	14,856	Sutter	7,677
		Tulare	264	SB	277	Tulare	5,356	Tulare	13,262	Tulare	2,451
		Ventura	74	Tulare	1,928	Yolo	129	Yuba	2,518	Yuba	3,712

July	lbs AI	Aug.	lbs AI	Sept.	lbs AI	Oct.	lbs AI	Nov.	lbs AI	Dec.	lbs AI
Contra Costa	1,018	Contra Costa	518	Contra Costa	266	Contra Costa	141	San Benito	7	Fresno	186
Fresno	2,632	Fresno	434	Fresno	749	Fresno	5	Yolo	1	Madera	280
Kings	325	Madera	158	Imperial	224	Imperial	363			San Benito	4
Madera	473	Modoc	483	Kern	395	Kern	2,003			Stanislaus	65
Modoc	715	San Benito	100	Monterey	42	Madera	23			Tulare	343
SJ	673	SJ	979	Riverside	401	Riverside	97				
Siskiyou	269	SLO	84	Sac.	5	Tulare	154				
Sutter	506	Siskiyou	383	SJ	386	Yolo	13				
Tulare	1,104	Tulare	286	Tulare	22						
Yuba	395	Ventura	75	Yolo	12						

[1]/ County Abbreviatons: Sac = Sacramento; SJ = San Joaquin; SB = Santa Barbara; SLO = San Luis Obispo

TABLE 5g: Monthly Applications of Methyl Parathion for 1996 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI	Feb.	lbs AI	March	lbs AI	April	lbs AI	May	lbs AI	June	lbs AI
Fresno	352	Alameda	173	Contra Costa	877	Fresno	5,123	Colusa	2,453	Butte	1,160
Madera	350	Contra Costa	391	Fresno	71	Kern	427	Fresno	8,248	Colusa	1,336
Riverside	81	Fresno	10	Kern	214	Kings	183	Kings	1,507	C.C.	1,518
San Benito s	2	Los Angeles	23	Madera	1,147	Madera	680	Lake	2,394	Fresno	2,620
Sutter	28	Riverside	797	Riverside	975	Riverside	112	Sacramento	4,851	Sacramento	817
Tulare	973	San Benito	5	San Benito	15	Sacramento	182	San Joaquin	2,727	SJ	575
Yuba	144	San Joaquin	758	San Joaquin	3,743	San Joaquin	276	Solano	1,404	Stanislaus	679
		Santa Clara	0	SLO	90	Tulare	6,843	Sutter	5,482	Sutter	7,551
		Stanislaus	16	SB	212	Yolo	299	Tulare	10,235	Tulare	4,009
		Tulare	104	Tulare	371	Yuba	221	Yuba	4,151	Yuba	4,568

July	lbs AI	Aug.	lbs AI	Sept.	lbs AI	Oct.	lbs AI	Nov.	lbs AI	Dec.	lbs AI
Butte	3,531	Butte	92	Colusa	159	Fresno	5,236	Imperial	12	Fresno	100
Contra Costa.	1,550	Contra Costa	465	Imperial	76	Imperial	614	Riverside	3,640	Riverside	43
Fresno	565	Madera	112	Kern	165	Kern	420	Yolo	3	Tulare	129
Madera	420	Modoc	269	Madera	50	Kingd	9				
Modoc	1,877	Riverside	226	Sac.	61	Riverside	295				
SJ	604	Sacramento	2,668	SB	303	Solano	18				
Siskiyou	624	SB	850	SJ	339	Tulare	85				
Sutter	487	SJ	368	Solano	168	Yolo	7				
Tulare	707	Solana	157	Suttere	190						
Yuba	496	Sutter	342	Tulare	155						

[1]/ County Abbreviatons: SB = San Bernardino; SLO = San Luis Obispo

TABLE 5h: Monthly Applications of Methyl Parathion for 1997 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI	Feb.	lbs AI	March	lbs AI	April	lbs AI	May	lbs AI	June	lbs AI
Fresno	37	Alameda	56	CC	667	Colusa	409	Butte	2,894	Butte	512
Riverside	146	CC	159	Fresno	151	Fresno	4,476	Colusa	2,295	CC	665
Tulare	17	Fresno	36	Kern	241	Kern	3,583	Fresno	10,339	Fresno	3,270
		Kern	1,615	Lake	41	Kings	804	Kings	2,865	Kern	1,148
		Riverside	1,663	Riverside	2,340	Lake	1,761	Lake	2,679	SJ	6,514
		Tulare	48	Sac.	102	Maderae	431	Merced	3,181	Solano	423
				SJ	2,227	Mendocino	893	Sac.	4,409	Stanislaus	965
				SLO	21	Riverside	402	Sutter	9,606	Sutter	4,110
				Tulare	359	SJ	966	Tulare	6,076	Tulare	2,192
						Tulare	5,865	Yuba	6,503	Yuba	1,170

July	lbs AI	Aug.	lbs AI	Sept.	lbs AI	Oct.	lbs AI	Nov.	lbs AI	Dec.	lbs AI
CC	629	CC	997	CC	100	Fresno	792	Imperial	76	Fresno	42
Fresno	607	Fresno	73	Fresno	152	Imperial	254	SJ	53	Stanislaus	41
Kings	334	Kern	418	Imperial	76	Kern	172			Tulare	29
Madera	647	Merced	26	Kern	8,038	Los Angeles	26				
SJ	5,061	Sac	171	Sac.	733	Madera	67				
Santa Cruz	199	SJ	2,046	SJ	301	SJ	35				
Stanislaus	651	SLO	157	Solano	336	Santa Cruz	17				
Sutter	602	Stanislaus	111	Sutter	243	Solano	327				
Tulare	679	Sutter	493	Tulare	1,682	Tulare	6,742				
Yolo	241	Tulare	1,954	Yolo	8	Yolo	6				

1/ County Abbreviatons: Sac = Sacramento; SJ = San Joaquin; SLO = San Luis Obispo

TABLE 5i: Monthly Applications of Methyl Parathion for 1998 by County[1]. (Pounds Active Ingredient)

Jan.	lbs AI
Kings	13
Riverside	484
Sutter	367
Tulare	39

Feb.	lbs AI
Fresno	13
Riverside	1,728
Tulare	24
Ventura	0

March	lbs AI
CC	556
Fresno	5
Kings	21
Riverside	1,232
SJ	1,047
Tulare	145

April	lbs AI
Butte	115
Fresno	2,856
Kern	2,648
Kings	149
Riverside	119
Sac.	405
SJ	126
Sutter	216
Tulare	8,827
Yuba	354

May	lbs AI
CC	2,272
Fresno	11,563
Lake	7,003
Mendocino	1,471
Sac.	6,300
S J	1,219
Sutter	1,214
Tulare	10,645
Yuba	1,099

June	lbs AI
CC	1,843
Fresno	3,629
Kern	2,491
Lake	4,726
Sac.	8,507
SJ	7,608
Stanislaus	1,698
Sutter	2,059
Tulare	1,494
Yuba	3,405

July	lbs AI
Butte	2,759
CC	3,832
Fresno	1,003
Kings	266
Madera	450
Merced	815
Stanislaus	11,686
SJ	1,527
Sutter	962
Tulare	1,833

Aug.	lbs AI
Butte	554
CC	2,308
Fresno	482
Kern	528
Kings	703
SJ	5,325
Solano	344
Stanislaus	839
Sutter	894
Tulare	783

Sept.	lbs AI
CC	464
Fresno	135
Imperial	127
Los Angeles	84
Merced	51
SJ	2,079
Solano	230
Stanislaus	58
Sutter	196
Tulare	193

Oct.	lbs AI
CC	230
Fresno	281
Madera	39
SJ	95
Tulare	24
Yolo	9

Nov.	lbs AI
Tulare	14

Dec.	lbs AI
Butte	7
Tulare	3

[1]/ County Abbreviatons: CC = Contra Costa; Sac = Sacramento; SJ = San Joaquin; SLO = San Luis Obispo

TABLE 6. Methyl Parathion Use by Commodity for 1990 through 1998 (Pounds Active Ingredient)

CROP	1990	1991	1992	1993	1994	1995	1996	1997	1998
ALFALFA	14,928	11,205	5,299	10,722	13,687	12,411	11,909	7,650	5,080
ALMOND	270	74	1,362	0	0	0	0	0	30
APPLE	2,446	1,901	5,420	12,542	4,092	10,180	7,273	17,721	27,141
APRICOT	0	0	0	0	0	576	0	0	1
ARTICHOKE	25	3,159	63	7	38	75	0	0	0
BEANS	1,365	1,112	1,345	166	175	61	703	688	1,128
CARROTS	485	76	1,729	237	0	0	0	0	0
CHERRY	0	0	0	0	0	0	0	0	26
COLE CROPS[1]	553	371	565	0	170	78	98	24	0
CELERY	353	65	0	0	0	7	0	0	0
CORN, SWEET	813	185	39	275	759	3,079	4,794	5,854	9,658
COTTON	4,592	3,115	1,428	144	312	1,177	1,328	144	71
GRAPES	309	274	2,378	11,374	13,587	21,279	9,210	19,569	9,269
LETTUCE	3,536	1,312	3,165	1,257	445	130	102	21	7
NECTARINE	515	2,422	6,360	18,070	15,822	15,774	14,921	12,900	12,466
NURSERY/OTHER	453	388	306	1,071	598	223	0	0	0
ONION	1,765	3,030	4,443	4,751	2,796	1,573	1,165	1,614	818
PASTURES/FORRAGE	0	65	517	40	46	75	5	0	0
PEACH	6,490	6,340	11,104	25,743	28,218	25,886	31,532	33,325	12,769
PEAR	29	84	374	714	1,932	5,157	13,022	13,169	34,945
PEAS	0	18	374	221	0	209	56	4	0
PEPPERS	0	20	29	0	96	0	0	0	0
PLUMS	813	4,319	13,415	20,099	23,422	20,165	16,638	15,452	15,633
POTATO	17	40	161	31	0	0	0	0	0
PRUNE	391	6	126	48	930	1,125	305	575	307
RICE	53,950	24,827	34,293	50,445	23,503	31,150	15,557	9,828	6,479
SMALL GRAINS[2]	2,521	1,783	2,878	8,126	1,696	1,738	3,326	764	49
SPINACH	1,101	905	669	591	735	831	337	123	52
SUGARBEET	1,415	2,819	2,903	2,328	1,880	482	741	871	146
TOMATO	5,198	2,402	2,714	499	195	110	328	244	0
WALNUT	0	0	0	0	0	0	0	14,454	32,451
TOTAL	**104,332**	**72,315**	**103,457**	**169,498**	**135,133**	**153,546**	**133,352**	**154,993**	**168,525**

[1] Cole Crops: Broccoli, Brussels Sprouts, Cabbage, Cauliflower, Kohlrabi, Mustard.
[2] Small Grains: Barley, Oats, Wheat

3.4. References

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4. PERSISTENCE AND FATE OF METHYL PARATHION IN THE ENVIRONMENT

4.1. Introduction

In the environment, methyl parathion may be degraded by hydrolytic reactions to less toxic compounds, or it may be activated by oxidative conversion to its more toxic oxon analogue, methyl paraoxon (Figure 1b, Figure 2). This section is devoted to the discussion of methyl parathion's fate in the environment. Most fate studies discussed below report the dissipation rate of the parent compound (methyl parathion), with little discussion of the actual disposition of methyl parathion in their studies, whether it dissipates, degrades, metabolizes or mineralizes.

In the atmosphere, fate reactions are usually accomplished through photolysis in the presence of natural atmospheric constituents or pollutants. In the presence of hydroxyl radicals and sunlight ($\lambda > 280$ nm), methyl parathion may be converted to methyl paraoxon (Cheminova Agro A/S. 1991). Methyl parathion can also be degraded into 4-nitrophenol, dimethylthiophosphoric acid and 2-methyl-4-nitrophenol by sunlight (Cheminova Agro A/S. 1988).

On plants, methyl parathion may volatilize, or may be converted to methyl paraoxon. The half life for methyl parathion's dissipation ranges from 1.6 hours to 38 hours and is affected by formulation, crop type, weather conditions, and the amount of time between application and sample collection (dissipation rate changes with time).

In soil, methyl parathion is degraded by biotic and abiotic factors. Soil type, temperature, and water content play important roles in this degradation. Recent research indicates that the presence of organic material—especially humic acids—or copper ions markedly affects methyl parathion breakdown. Little information exists showing the significance of methyl parathion's binding to wind borne dust particles and their role in potential atmospheric loading or translocation of methyl parathion.

In water, methyl parathion is also degraded by biotic and abiotic factors. Salinity, temperature, and turbidity all affect the rate of methyl parathion's breakdown. The presence of sediment or suspended soil particles in water significantly increases methyl parathion's breakdown. Centrifugation, or autoclaving water significantly decreases methyl parathion's breakdown supporting the hypothesis that micro-organisms play an important role in the breakdown of methyl parathion in water.

4.2. Fate in the Atmosphere

Apart from the effects of formulation, the degree of pesticide dispersion depends upon the magnitude of drift during application and post application volatilization. During application, the extent of drift is primarily affected by droplet size created by the applicator nozzle. Weather conditions such as wind speed, ambient temperature, and humidity may also influence the degree of drift. Although some volatilization may occur during application, the degree of post-application dispersion is largely a result of volatilization from foliar and soil surfaces, and conversion of methyl parathion to methyl paraoxon. Volatilization of methyl parathion from flooded rice fields occurs, but is considered of minor importance to the methyl parathion load in air in rice-growing areas. The low rate of volatilization is attributable to methyl parathion's relatively low Henry's Law constant and it's rapid rate of hydrolysis in rice field-water Seiber *et al.* (1989). Thus while methyl parathion may volatilize from water, this fate process should not play a significant role in methyl parathion's dissipation from rice field water.

Following foliar and/or soil surface type applications of methyl parathion, volatilization remains the most likely path for its entry into the atmosphere (Willis *et al.* 1985). Humidity, temperature and wind speed all affect the extent of this volatilization (Lewis and Lee, Jr., 1976). Volatilization increases as wind speed increases through two mechanisms: 1) increasing the concentration gradient between plant or soil surfaces and air; and/or 2) through a disruption of boundary layers at foliar or soil surfaces (Willis *et al.* 1985). For methyl parathion and other pesticides of comparatively low volatility, the disruption of the boundary layer and its corresponding decrease in size enhances volatilization, thereby increasing movement of pesticide molecules into the atmosphere (Hartley and Graham-Brice, 1980).

Additionally, vapor pressure affects the movement of pesticides from soil, plant surfaces and water into air. Vapor pressure of a pesticide increases as temperature increases, which in turn increases volatilization rates (Spencer *et al.*, 1979). Ware *et al.* (1980) found that evening application of methyl parathion resulted in increased persistence. They attributed this increase in persistence to lower volatility during the cooler hours of evening and night, leading to increased adsorption of methyl parathion onto foliar surfaces.

Other weather conditions have been demonstrated to markedly affect the levels of certain pesticides in air. Rainfall can decrease ambient air concentrations of pesticides by washing them out of the air (Stanley *et al.*, 1971; Willis *et al.*, 1985). Temperature inversions reduce air movement, decrease the general dispersion of pesticides as vapors or as particulates, resulting in unusually high ambient air concentrations (Lewis and Lee, Jr., 1976). In some cases, pesticide concentrations can be enriched in fog water droplets to levels several thousand fold greater than concentrations predicted based on the pesticides physiochemical properties (Glotfelty *et al.*; 1987). Such concentration enhancement in fog may contribute to off-site movement. Turner *et al.* (1989) showed that both wet (fog) and dry deposition of pesticides on vegetation occurred within and beyond an established 0.25 mile buffer zone surrounding fields to which pesticides had been applied.

4.2.1. Atmospheric Reactions

While the atmospheric reactions of methyl parathion have not been extensively studied, one would expect them to be to be similar to those of ethyl parathion. The structural difference between these two pesticides is the presence of two methoxy groups (methyl parathion) or two ethoxy groups (ethyl parathion) attached to the phosphorous atom of 4-nitrophenyl phosphorothioate. Conversion of ethyl parathion to ethyl paraoxon in the atmosphere depends on several variables. One, whether the pesticide exists as a vapor or is adsorbed to particulate matter (Moilanen *et al.*, 1975; Woodrow *et al.*, 1977), and two, whether sunlight and atmospheric pollutants are present (Spear *et al.*, 1978; Spencer *et al.*, 1980; Woodrow *et al.*, 1978). These environmental variables may play similar roles in the conversion of methyl parathion to methyl paraoxon.

Studies of the potential atmospherically-important gas-phase reactions of a series of trimethyl phosphorothioates, compounds structurally similar to methyl parathion, have shown that these organophosphorus compounds do not react with ozone or with nitrate (NO_3) radicals, but do react with the hydroxyl (OH) radical (Atkinson et al.1988, Goodman et al., 1988). Reactions of the OH radical with $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$ were found to lead to the formation of the corresponding oxon in 28% and 13% yield, respectively (Atkinson et al., 1989). Based on structure-reactivity relationships developed from the available OH radical rate constant data-base (Kwok and Atkinson, 1995), the half-life of gaseous methyl parathion can be calculated to be approximately 1 hour at a reasonable mid-day OH radical concentration of 3 $x10^6$ molecule/cm, with the half-life being inversely proportional to the OH radical concentration. The formation of the oxons from the OH radical reactions with $(CH_3O)_3PS$ and $(CH_3O)_2P(S)SCH_3$ are analogous to the observation of methyl paraoxon in the ambient atmosphere after application of methyl parathion, although the actual route to methyl paraoxon formation has, to date, not been determined. In the gas phase, methyl paraoxon is predicted to be significantly more persistent than methyl parathion, using the structure-reactivity estimation method of Kwok and Atkinson (1995).

Two studies have explored the effect of simulated sunlight on methyl parathion's atmospheric stability and conversion to methyl paraoxon (Cheminova Agro A/S. 1991; Cheminova Agro A/S. 1988). The proposed atmospheric half-life for methyl parathion varies from 8 to 18 hours depending on wavelength tested, atmospheric conditions and the presence of OH radicals. The rate constant k_{OH} (methyl parathion was calculated to be approximately $30(\pm 15)x10^{-12}$ ccm/molecule second, resulting in a value of 12.8 hours for the half-life in the presence of and average OH concentration and a value of 18.5 hours for the chemical lifetime.

4.2.2. Effects of fog

To determine the distribution of pesticides between fog-water and interstitial air, Glotfelty *et al.* (1987) sampled 12 pesticides and their metabolites during heavy fog-events in rural areas of the Beltsville, Maryland, and the Central Valley of California. For each pesticide, they measured the concentrations in air and fog-water, and calculated each pesticide's distribution ratio. Comparing these values to literature values, they showed that for some pesticides the air:fog-water ratio was far less than expected, indicating that concentrations of these pesticides in fog-water had been enriched. For methyl parathion (detected only in one Beltsville sample), the air:fog-water ratio indicated no enrichment.

Glotfelty *et al.* (1987) hypothesized that a pesticide's enrichment in fog-water could provide a mechanism whereby chemicals capable of entering the atmosphere, may move to surfaces some distance away. Pesticides that could move into fog water would then be transported off site and deposited on non-target vegetation. Thus, both pesticide-laden fog particles and contaminated non-target vegetation could possibly become major sources of incidental exposure.

Although, Glotfelty *et al.* (1987) reported only one detection of methyl parathion in fog-water, they determined that the air:fog-water distribution ratio was actually less than literature values. It was not determined whether the air:fog distribution was attributable to the difference in fog pH (2.4 Beltsville, 5.1-7.0 California), or to other unknown factors. However, methyl parathion is not commonly used in the Central Valley during months when fog-events occur (Tables 5a - 5f). This fact suggests that fog may not play a major role in the atmospheric translocation of methyl parathion. However, if use were to increase during periods of fog-events, methyl parathion's translocation may increase during winter months.

4.3. Fate on Plants

Dissipation of methyl parathion from foliar surfaces has been measured in field studies (Smith *et al.* 1987; Ware *et al.* 1974; Ware *et al.,* 1980, Willis *et al.* 1985). Dissipation was measured via the loss of methyl parathion itself, without identifying if the loss was due to breakdown, dissipation or other factors. Ware *et al.* (1974) determined methyl parathion's volatilization ranged from 4.8 hours to 38 hours, and that application time, rate, crop type, and weather variables played important roles. Willis *et al.* (1985) reported that the disappearance half–life of methyl parathion was 2.4 hours. Smith *et al.* (1987) reported half–life values of 4.4 and 5.4 hours from foliar surfaces following applications of an emulsifiable concentrate formulation.

Weather variables may play important roles in the dissipation of methyl parathion from foliar surfaces. Kido *et al.* (1975) showed that 90% of the surface residue of methyl parathion was lost within 1 day of application, compared to a 97 % reduction of the surface residue in plots receiving irrigation water via overhead sprinklers. If sprinkler irrigation occurred on the day following methyl parathion application (or later), there was only an extremely slight decrease in methyl parathion concentrations (96%:97% non-irrigated:irrigated). They concluded sprinkler irrigation played only a slight role in methyl parathion's dissipation from grape leaves. However, Cohen and Steinmetz (1986) found that the loss of methyl parathion (due to wash-off) accelerated when artificial foliar surfaces were exposed to simulated rainfall such as sprinkler irrigation. Finally, Youngman *et al.* (1989) showed that the herbicidal effects of p-nitrophenol (a breakdown product of methyl parathion) were substantially decreased due to rainfall or sprinkler application. They hypothesize that the water solubility of p-nitrophenol (1.6 g/l) was the responsible factor.

Reaction rates for the conversion of methyl parathion to methyl paraoxon and the subsequent buildup in methyl paraoxon on leaf surfaces has been shown in field studies to occur twice as rapidly as reaction rates for the conversion of ethyl parathion to ethyl paraoxon and ethyl paraoxon's subsequent buildup (Ware *et al.*, 1973). Twelve hours after application of equal amounts of methyl or ethyl parathion, the concentration of the corresponding oxon's surface residues was 3.31 mg/cm^2 for methyl paraoxon and 2.75 mg/cm^2 for ethyl paraoxon. Simultaneously, the air concentration of methyl paraoxon was 0.12 mg/cm^2, while the air concentration of ethyl paraoxon was 0.04 mg/cm^2.

Extending their 1973 field studies, Ware *et al.* (1974) reported that by 24 to 30 hours after application, methyl parathion levels had decreased from 1.6 to 0.9 mg/m^2 of foliar surface. Similarly, methyl paraoxon levels decreased to less than 0.05 mg/m^2 by 24-hours. Although Ware *et al.* (1974) did not calculate a conversion half–life, data presented by Winterlin *et al.* (1982) suggest that the half–life for converting methyl parathion to methyl paraoxon was shorter than the estimated half–life of 8.5 days for the conversion of ethyl parathion to paraoxon on foliar surfaces. Thus, methyl parathion is expected to dissipate from foliar surfaces faster than ethyl parathion because methyl parathion is more volatile, and because it is converted to its oxon more rapidly.

Methyl parathion has also been shown to negatively affect plant growth (Leigh, 1963; Gipson, 1974), and is still used on cotton despite studies indicating it's negative effect on growth (Bradley and Corbin, 1974). Youngman *et al.* (1990) reported a strong tendency toward less boll retention in plots treated four or more times per season. These authors reported that four applications of methyl parathion significantly reduced mesophyll conductance, number of mature and open bolls per plant, weight of lint cotton at harvest, and the dry weight accumulation of fruiting forms, among other negative effects. Methyl parathion was one of many pesticides shown to negatively affect the physiology, growth, and yield of a wide variety of crop plants (Ferree, 1979; Jones *et al.*, 1980).

In lettuce, similar reductions in yield have also been reported (Youngman *et al.*, 1990). Methyl parathion was applied at a rate of one pound AI/acre, to two-week old lettuce seedlings grown under field and glasshouse conditions. Applications were made once per week for four weeks before sampling occurred. Significant decreases in whole-plant dry weight, and leaf area was observed. Repeating the experiment with p–nitrophenol—0.5 lb AI/acre—produced similar results. The herbicidal affect of methyl parathion on plants has been attributed to its breakdown to p-nitrophenol, which is chemically similar to the herbicide DNOC (2–methyl–4,6–dinitrophenol) (Johnson *et al.*, 1983).

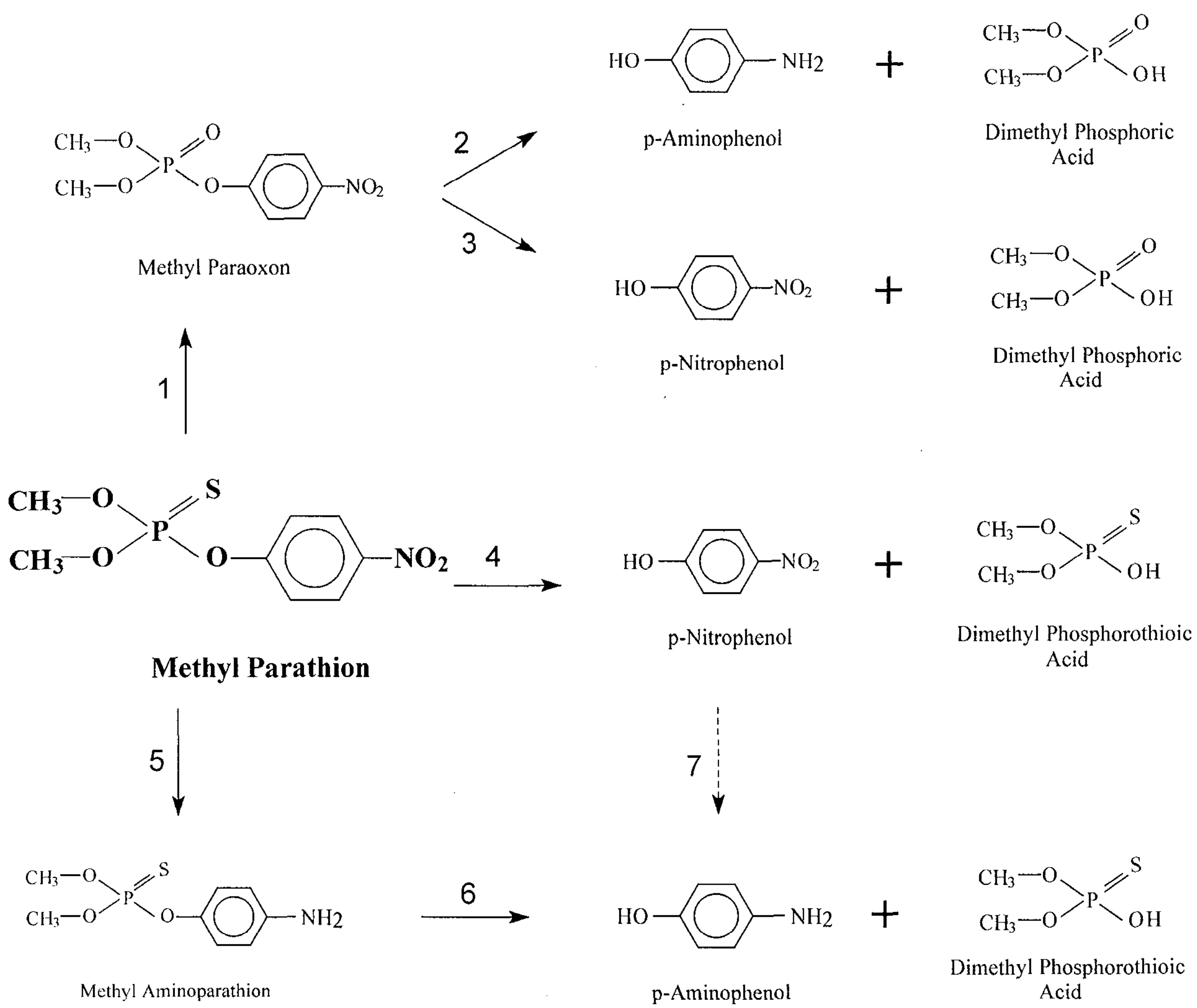
4.4. Fate in Soil

Methyl parathion completely degrades in soil, generally following one of two pathways (Figure 5). The first pathway involves the hydrolytic conversion of methyl parathion to p-nitrophenol and dimethyl phosphorothioic acid. The second pathway proceeds via reduction of methyl parathion's nitro group to an amine, producing methyl aminoparathion; methyl aminoparathion is then hydrolytically degraded to p–aminophenol and dimethyl phosphorothioic acid. These pathways are also responsible for the conversion of methyl paraoxon. Once methyl parathion is hydrolyzed to methyl paraoxon, further degradation proceeds by either hydrolysis—producing p–nitrophenol and dimethyl phosphoric acid directly, or via nitro–group reduction—producing methyl aminoparaoxon, which is then hydrolytically degraded to p–aminophenol and dimethyl phosphoric acid.

Degradation of methyl parathion and methyl paraoxon is microbially mediated, and proceeds by the hydrolysis in soil under aerobic conditions (Adhya *et al.*, 1981b; Gerstl *et al.*, 1985; Lewis *et al.*, 1985; Megharaj *et al.*, 1994; Ou and Sharma, 1989; Pritchard *et al.*, 1987; Sharmila *et al.*, 1988, 1989; and Wolfe *et al.*, 1986). Degradation via nitro–group reduction occurs in sediments and flooded soils which are anaerobic (Adhya et al. 1987; Sharmilla, *et al.*, 1988, 1989). The importance of soil–microbes in methyl parathion's degradation is amply demonstrated by markedly reduced rates of methyl parathion degradation in autoclaved soils (Sharmila *et al.*, 1988, 1989), and by reduced degradation rates in the aqueous phase of flooded soils and river–bed sediments when the soil component was removed via centrifugation (Adhya et al. 1987, Brahmaprakash *et al.*, 1987; Wolfe *et al.*, 1986). Kodoma and Kuwatsuka (1980) reported that complete degradation of methyl parathion in river–water occurred within 72 hours. However, boiling river–water drastically affected the degradation of methyl parathion; after 72 hours, only four percent of methyl parathion was degraded in river–water that had been boiled. The authors hypothesize that boiling river–water destroyed any micro-organisms present.

FIGURE 5.

Pathways for Methyl Parathion's Degradation in the Environment



1) Hydrolytic reaction in soil and water with hydroxide ion. Photolytic reaction in air with hydroxyl radicals.
2) Nitro–group reduction: Anaerobic reaction in strong reducing soils, high in organic matter, or in acidic soils.
3) Hydrolytic reaction with OH^- on plants, in soil and water (sediment). Aerobic; moist soils and certain flooded soils; soils at 35°C; soil micro–organismal mediated; high or low organic material; neutral–basic conditions.
4) Hydrolytic reaction with OH^-: Occurs in air, on plants, in soil and water. Aerobic; moist soils and certain flooded soils; soil micro–organismal mediated; high or low organic material; neutral–basic conditions.
5) Nitro–group reduction: Occurs in flooded soils at and below 25°C, soils high in organic matter, or soils with strong reducing conditions.
6) Hydrolytic reaction with OH^-: Occurs in air, on plants, in soil and water. Aerobic; moist soils and certain flooded soils; soils at 35°C; soil micro–organismal mediated.
7) Nitro–group reduction: p–nitrophenol converted to p–aminophenol. Possible reaction, unlikely in most conditions.

Ou and Sharma (1989) reported the existence of a *Bacillus* species which could utilize methyl parathion as its sole carbon source. Using ring–position radio–labeled ^{14}C, they were able to show that methyl parathion was converted to $^{14}CO_2$ within 24–hours, indicating that the *Bacillus* species was able to mineralize methyl parathion completely. However, in a separate mixed bacterial media, they isolated a *Pseudomonas* species which degraded p-nitrophenol to CO_2 and H_2O, but which could not degrade methyl parathion itself. In this mixed media, an extraneous source of carbon (glucose or a yeast extract) was needed for methyl parathion's complete mineralization. The authors concluded that the *Bacillus* species was able to completely metabolize methyl parathion, and that a mixed bacterial culture was able to mineralize methyl parathion in the laboratory, indicating that cometabolism may be an important pathway for methyl parathion's degradation in soil.

Lewis et al. (1985) described a multiphasic system responsible for the degradation of methyl parathion in soil. This multiphasic system was isolated from a soil bacterium, (*Flavobacterium species*). Pure cultures of this soil bacterium were inoculated onto several soils pre-incubated with different concentrations of methyl parathion. Soils were sampled 20 minutes and eight hours following inoculation, and the concentrations of methyl parathion measured. Results indicated that (*Flavobacterium species*) possesses at least two separate systems for degrading methyl parathion, and suggest the strong possibility for a third. The first methyl parathion transformation system, identified as System I, possessed high-affinity for methyl parathion, but low-capacity for transformation, and operated at low concentrations (7 µg/L to 48 µg/L) of methyl parathion. The second methyl parathion transformation system, identified as System II, possessed lower affinity for methyl parathion, but operated at higher (175 µg/L to 3,700 µg/L) methyl parathion concentrations.

Lewis *et al.* (1985) also found that at some concentrations (≈52 µg/L), degradation initially proceeded via System II switching to System I, after time as concentrations dropped. However, if the original concentrations were high (≈175+ µg/L) methyl parathion's degradation proceeded solely via System II. The authors concluded that the degradation of methyl parathion in natural systems is microbially mediated and probably followed multiphasic kinetic systems.

In a laboratory study of soil and sediment suspensions, under anaerobic and strongly reducing conditions, the half–life of methyl parathion ranged from 0.75 – 36 minutes (Wolfe *et al.* 1986). Under these conditions methyl parathion was reduced to methyl aminoparathion, and p-nitrophenol was not observed. Methyl parathion's half–life ranged from 596 – 3700 minutes in the aqueous phase after the soil component was removed by centrifugation, again indicating the importance of soil-microbes to methyl parathion's degradation. Under strong reducing conditions, soil pH did not appear to be a significant factor in methyl parathion's conversion to methyl aminoparathion.

4.4.1. Factors Affecting the Degradation of Methyl Parathion in Soil.

Soil microbes are putatively the major force responsible for methyl parathion's breakdown in soil. Other factors which affect methyl parathion's degradation (possibly through effects on the soil microbiota) are:

- Soil temperature (Baker and Applegate, 1970; Sharmila *et al.*, 1988, 1989)
- Soil water content (Adhya, *et al.*, 1981; Brahmaprakash *et al.*, 1987; Ou, 1985; Ou *et al.*, 1983;)
- Agronomic practices, including irrigation, fertilizers, pesticide applications, and the addition of organic material (Gerstl and Helling, 1985).

The effects of these factors on the rates and pathway of methyl parathion's degradation in soil are discussed below.

4.4.1.1. Soil Temperature

Sharmila *et al.* (1987; 1989) observed that the rate and pathway of methyl parathion degradation in flooded soil was markedly affected by soil temperature. Estimated half lives of methyl parathion degradation (determined by the amount of methyl parathion remaining) were 40 days, 2–3 days, and one day in soils incubated at 6 °C, 25 °C, or 35 °C respectively. The authors determined that nitro–group reduction was the primary pathway for methyl parathion degradation in soil at 25 °C, because methyl–aminoparathion was the only breakdown product detected. In soil at 35 °C, breakdown followed both hydrolytic and nitro–group pathways, with twice as much p–nitrophenol detected as methyl aminoparathion. No breakdown products were detected in soils kept at 6 °C, although the amount of methyl parathion present decreased over time.

To isolate the influence of temperature on the biotic and abiotic pathways of methyl parathion degradation, the authors compared the rates and principal degradation products in autoclaved soil (no microbial component) and untreated control soil (with microbial component). Incubating both soils at 35 °C, they found that only 15 percent of the methyl parathion degraded after six days on autoclaved soil. In the untreated control soil, almost eighty percent of methyl parathion had degraded within two days, and methyl parathion was not detected after four days. In autoclaved soil, the only breakdown product detected was p–nitrophenol while both p–nitrophenol and methyl aminoparathion were detected on control soil (Sharmilla, *et al.*, 1988). These findings support the hypothesis that soil microbes dominate methyl parathion's breakdown in soil.

The presence of humic acids (Almendros, 1995), rice straw (Sharmila *et al.*, 1989), and general organic matter (Ou and Sharma, 1989; Sharmila *et al.,* 1989; Wolfe *et al.*, 1996) in soil, have been shown to affect methyl parathion's degradation. In essence, increased organic matter, irrespective of source, increases methyl parathion's degradation to methyl aminoparathion. However in some soils, notably those whose pH is near neutral or basic, the dominant breakdown product is p–nitrophenol.

4.4.1.2. Soil Water Content

Soil water content influences the rate and pathway of methyl parathion degradation in soil (Ou, 1985; Ou *et al.,* 1983). Dry soil is aerobic but has low microbial activity; these conditions lead to a low rate of conversion of p–nitrophenol to p-aminophenol and correspondingly a lower rate of mineralization of methyl parathion. Microbial activity increases as soil moisture increases so that at intermediate soil water concentrations, the rate of methyl parathion mineralization is higher than under dry conditions. Finally, when the soil is near or at the saturation point, the soil may become anaerobic, mineralization slows, and methyl parathion is degraded by nitro–group reduction (Adhya *et al.* 1987).

In laboratory experiments, Adhya et al. (1987) saturated several soil types with water prior to adding methyl parathion. They showed that methyl parathions breakdown (via analysis of breakdown products) proceeded via nitro–group reduction. However, (Sharmila *et al.* 1989) showed that the breakdown of methyl parathion on some flooded soils, such as Sukinga (laterite soil, pH 6.9, organic matter 0.62%, 0.04% total nitrogen), exclusively followed hydrolytic pathways . Both studies showed that increasing soil temperature increased the rate of methyl parathion's breakdown.

Brahmaprakash *et al.* (1987) showed that methyl parathion's breakdown occurred much faster in flooded alluvial (pH 6.5, organic matter 1.6%, total nitrogen 0.1%) soils than non–flooded (60% of water–holding capacity) alluvial soils. Soils were maintained in the laboratory at 28 °C for 15 days to allow stabilization of the microbial component before addition of methyl parathion. In all soils, the major pathway for methyl parathion's degradation during the first seven days was hydrolytic; as indicated by the 10–fold greater production of p–nitrophenol than methyl aminoparathion. However, in flooded alluvial soils, this ratio fell to 5:1 after 14 days, 2:1 after 28 days, and 1:1 after 56 days. In non-flooded soils the ratio of the production of the two degradation products (p-nitrophenol:methyl aminoparathion) remained relatively constant, varying between 10:1 and 7:1, over the course of the study. The overall rate of methyl parathion's disappearance was higher in flooded soils than in non–flooded soils.

4.4.1.3. Agronomic Practices

Agronomic practices affect the fate of methyl parathion in soil (Gerstl and Helling, 1985), mainly through the addition of organic matter or adjuvants which affect soil organic matter content, pH, and water retention capacity. Irrigation or flooding of fields may also enhance methyl parathion's degradation, and will influence the degradative pathway and end products produced affecting the pathway and rate of degradation (Adhya *et al.*, 1987; Brahmaprakash *et al.*, 1987; Ou, 1985; Ou *et al.*, 1983; Sharmila *et al.*, 1989).

4.5. Fate in Water

In California, methyl parathion is applied to flooded rice fields, by aircraft, during May and June (Table 5a - 5f; Hunter, 1995). Movement of methyl parathion into the atmosphere from rice field water is considered minor because of methyl parathion's relatively low Henry's constant (Lyman *et al.* 1990), and because of the rapid hydrolytic conversion of methyl parathion to methyl paraoxon. Dortland (1980) reported a half–life of 78 to 99 hours for methyl parathion in aquarium water which contained bottom material and water plants, compared to a half–life of 231 hours in aquarium water alone. Dortland (1980) hypothesized that microbial transformation rather than volatilization played the key role in the dissipation of methyl parathion in water. McChesney and Seiber (1986) observed a half–life of 35–40 hours for methyl parathion in rice field water, similar to that reported by Dortland (1980). McChesney and Seiber (1986) observed that the air levels of methyl parathion above these fields, although low, were consistent with concentrations expected based on vapor pressure and Henry's Law constant (Table 1). They concluded that hydrolytic and microbial degradation of methyl parathion were more important factors contributing to methyl parathion's dissipation than volatilization (McChesney and Seiber 1986; Seiber *et al.* 1979).

Seiber and McChesney (1987) measured methyl parathion concentrations in air following an application to a flooded rice field located in Glenn County, California. A single air sampler was placed 15.5 meters north of the edge of the field, with the prevailing winds toward the sampling device (from the southeast), and samples were collected for 1.5-hour time periods. Following the application of an unknown amount of methyl parathion, the resultant airborne methyl parathion concentration averaged 1,095 ng/m^3 (101.8 ppt) ranging from 1,030 ng/m^3 to 1,160 ng/m^3 (95.8 ppt and 107.9 ppt respectively). This concentration represented a 60–fold increase in airborne methyl parathion as compared to the background level of 18 ng/m^3 (1.7 ppt) and occurred between one and seven hours after application. These concentrations dropped rapidly over the next two days to 48 ng/m^3 to 51 ng/m^3 (4.5 ppt to 4.7 ppt) (Table 7).

Data from Dortland (1980), and McChesney and Seiber(1986) indicate that the volatilization from water, while important, is not the dominant process for methyl parathion's disappearance from rice field waters. Both authors based their observations on methyl parathion's relatively low Henry's Law Constant (Table 1), and its relatively fast rate of hydrolysis. They concluded that photochemical or microbial degradation processes may play more significant roles in the disappearance of methyl parathion from rice field water.

Other authors have shown the importance of microorganisms (Newton *et al.* 1990), copper ions (Dowling and Lemley, 1995) cyclodextrins (Kamiya *et al*; 1995: Kamiya *et al.* 1992), humic acids (Benson and Long; 1991) and general organic materials (Kadlec and Benson, 1995) on the degradation of methyl parathion in water.

TABLE 7.

Airborne Concentrations of Methyl Parathion Reported in the Literature: Areas Associated with Pesticide Applications

	Formulation Type				
	Emulsifiable Concentrate		Micro Encapsulated		
Day	ng/m³	ppt	ng/m³	ppt	Comments
0	7,400	688.2	3,800	353.4	Jackson and Lewis 1979.[1]
1	3,300	306.9	330	30.7	
3	580	53.9	110	10.2	
6	36	3.4	25	2.3	
6	54	5.0	19	1.8	
9	13	1.2	16	1.5	

1 Concentrations were measured in samples collected at row ends, less than 1 meter from treated tobacco plants during summer in North Carolina. Sampling duration, 1- to 2- hours.

Day	Hours after Application	Detected Residue ng/m³	ppt	
0	1	1,030	95.8	Seiber and McChesney 1987.[2]
0	7	1,160	107.9	
2	48	51	4.7	
2	55	48	4.5	

2 Samples collected 15.5 meters from the border of a treated-flooded rice field during May. Methyl parathion application occurred on the 5th day of a 7-day study. Concentrations of methyl parathion were 100 fold greater than concentrations measured on previous days. Sample duration 1.5 hours.

Micro-organisms play a role in the degradation or transformation of methyl parathion, the rates of which depending on physical, chemical and biological conditions of the system (Newton *et al.* 1990). Using microbial rich sediment and floating microbial mats, collected from lakes, streams, and rivers in Georgia and Florida, they determined that the average value for methyl parathion's half-life, was 29 hours for microbial rich sediment, but only 6.9 ($\pm$1.2 SE) hours for microbial mats. Transformation of methyl parathion proceeds through ester hydrolysis (Paris *et al.* 1986; Paris *et al.*, 1984); rates were directly related to methyl parathion concentrations, indicating a pseudo first-order mechanism. Abiotic transformation was evaluated by use of autoclaved controls, and accounted for less than five-percent of methyl parathion's transformation. Their data indicate that biotic breakdown mechanisms in natural waters dominate methyl parathion's dissipation.

Commercial pesticide applicators, growers and private farmers, generate significant volumes of pesticide-contaminated rinsates and wastewaters (Seiber, 1988). The generation of methyl parathion-contaminated wastewater is of concern because improper disposition of wastewater can lead to environmental contamination. Several authors have shown that methyl parathion can be rapidly degraded via the addition of Fenton's reagent (Dowling and Lemley, 1995; Pignatello and Sun, 1995; Lipczynska-Kochany, 1991). The mechanism of Fenton's reaction is due to the generation of hydroxyl radicals via transformation of Fe^{2+} to Fe^{3+} in the presence of hydrogen peroxide. Lipczynska-Kochany (1991) showed that the degradation of methyl parathion proceeds through methyl paraoxon, p-nitrophenol, and continues until all aromatic products are removed, with a half-life of 20 minutes. Half-lives decreased to 5.1 to 5.3 minutes upon addition of Cu^{2+} ions at 2.9×10^{-4} M. Addition of methanol (representative of organic adjuvants present in formulated pesticide products) decreased the half-life to approximately 70 hours.

4.6. Airborne Levels of Methyl Parathion Reported in the Literature

4.6.1. Airborne Levels During and After Application

Many factors may contribute to airborne concentrations of methyl parathion during and following application. Some factors are formulation (Jackson and Lewis, 1978), amount of pesticide applied (Ware *et al.*, 1973; 1974), size of area treated (Akhmedov, 1969), season of application, and/or method of application. Volatilization of methyl parathion from plant surfaces following application may also contribute to it's presence in the atmosphere.

Formulation type may affect air concentrations of methyl parathion (Jackson and Lewis, 1978; 1979). Tobacco fields in North Carolina were treated with either an emulsifiable concentrate or a microencapsulated formulation of methyl parathion at a rate of 1 lb/acre. Following application, air samples collected from fields treated with the emulsifiable concentration contained higher levels of methyl parathion than samples collected from fields treated with the microencapsulated formulation, 7,400 ng/m^3 (688 ppt) and 3,800 ng/m^3 (353 ppt), respectively. Dissipation from both fields was moderately rapid and concentrations measured above either field nine days after application was not significantly different at 13 ng/m^3 (1.2 ppt) for the emulsifiable concentrate treated field and 16 ng/m^3 (1.5 ppt) for the microencapsulated treated field. Following light rainfalls on days six and eight, methyl parathion concentrations in air were reduced. The authors concluded that formulation does affect the atmospheric concentration of methyl parathion.

The application rate of methyl parathion also affects airborne concentrations (Seiber and McChesney, 1989; Ware *et al.*, 1973). Ware *et al.* (1973) measured air concentrations of methyl parathion within cotton fields for thirty minutes following application. Samples were collected by attaching air samplers to workers who re–entered the treated field 3 minutes after the application was completed. The average methyl parathion concentration was 1,243 ng/m^3 (115.6 ppt) and ranged from 932 ng/m^3 to 1554 ng/m^3 (86.7 ppt to 144.4 ppt). Air concentrations within a field, as reported by Ware *et al.* (1973) were three orders of magnitude greater than ambient concentrations reported by Seiber and McChesney (1989), and twice as high as air concentrations measured 17 meters from a field to which methyl parathion had been applied (ARB 1989).

The air concentration of methyl parathion may also be related to the area treated. Akhmedov (1969) reported that airborne concentrations of methyl parathion measured 500 meters away from treated fields ranged from 55 to 80 μg/m^3 (5.1 to 7.4 ppb) for a 3.0 ha (7.5 acre) field and ranged from 153 to 330 μg/m^3 (14.1 to 30.4 ppb) for a 5 ha (11 acre) field. These concentrations are higher than values reported by other authors. Since the amount applied was not reported it is possible that the application rate of methyl parathion differed between fields. Further observations reported by Akhmedov (1969) include: 1) the concentration of methyl parathion in air was related to the distance of the sampler from the application site and the time that had elapsed since application; 2) methyl parathion concentrations observed during the day are higher than those seen in the morning or evening; 3) windy conditions increase dispersal and lead to lower air concentrations of methyl parathion; and 4) relative humidity was not a factor influencing the atmospheric concentration of methyl parathion.

4.6.2. Ambient Airborne Levels

For the purposes of this discussion, the term "ambient airborne concentrations of methyl parathion" is used to refer to concentrations of methyl parathion in air that are not associated with a specific application. Ambient concentrations of methyl parathion have been measured at different rural and urban sites, remote from the original application sites. Five studies are summarized in Table 8 and are discussed below. Samples were also analyzed for the presence of methyl paraoxon.

Stanley *et al.* (1971) monitored for the presence of 19 pesticides, including methyl parathion, in ambient air. Monitoring stations were situated at urban and rural sites in eight states. Two urban sites in California, located near the cities of Fresno and Riverside, were included. Either 12- or 24-hour samples were collected for 14 days per month over seasons thought to reflect both high and low pesticide usage. Although methyl parathion was not detected at the California sites, it was found in samples taken at rural sites in Alabama, Florida, and Mississippi. The highest measured concentration of methyl parathion was 148 ng/m^3 (13.8 ppt). Stanley *et al.* (1971) concluded that airborne concentrations of methyl parathion were far below those levels that might significantly add to the total human intake from dermal and/or oral sources. In addition, these investigators found no correlation between rainfall and air concentrations of methyl parathion.

Kutz (1976) reported the results of an ambient air monitoring study conducted over the three year period 1970-1972. Sites were chosen because of their proximity to agricultural areas where pesticides are used, indicating the potential for high ambient pesticide concentrations. Samples were collected over 24-hour periods, and concentrations represent methyl parathion residues in 45 m^3 to 74 m^3 of air. The number of samples collected ranged from 11 (Alabama, 1971) to 75 (Tennessee, 1970). Methyl parathion was one of the 32 pesticides detected in rural and suburban ambient air at sites located in Alabama, Arkansas, Illinois, Kansas, Kentucky, Louisiana (1971,1972), Maine, Montana, New Mexico (1971,1972), North Carolina, Ohio, Oklahoma, Oregon, South Dakota, and Tennessee (1970-1972).

TABLE 8.

Airborne Concentrations of Methyl Parathion Reported in the Literature: Ambient Airborne Concentrations

Location	SAMPLES Total Number	# Testing Positive	Maximum Value ng/m³	Maximum Value ppt	Mean of Positive Samples ng/m³	Mean of Positive Samples ppt
Mississippi[a]	42	17	148	13.8	29	2.7
Mississippi[b]	98	40	129	12.0	—	—
Alabama[b]	90	9	30	2.8	—	—
Florida[b]	99	3	5	0.5	87	8.0
Various[c]	143	15	160	14.9	—	—
Various[d]						
1970	787	82	279	26.0	16	1.5
1971	658	54	65	6.1	4	0.4
1972	1,025	145	105	9.8	12	1.1
Mississippi[e]	156	—	2,060	191.6	91	8.4
1972	52	—	217	20.2	79	7.3
1973	52	—	791	73.6	161	14.8
1974	52	—	341	31.7	56	5.2

a/ Stanley et al., 1971. Results from rural Mississippi locations. Maximum methyl parathion concentrations were associated with adjacent pesticide applications.

b/ Stanley et al., 1971. Rural locations.

c/ Kutz, 1983. Monitoring results from 1980, from 10 sites in 8 states. Maximum value reported was via the detection of p–nitrophenol, without differentiation between ethyl and/or methyl parathion.

d/ Kutz et al., 1976. Monitoring results from 16 states.

e/ Arthur et al., 1976. Weekly samples taken from 1972 - 1974. Maximum positive values are monthly averages.

— Data not available

Methyl parathion was detected in 10.4 percent of the samples collected in 1970, in 8.2 percent of the samples collected in 1971, and in 14.1 percent of the samples collected in 1972. The maximum concentrations of methyl parathion varied by location, and were 278.5 ng/m³ (25.9 ppt), Oklahoma 1970; 65.1 ng/m³ (6.1 ppt), Tennessee 1971; and 105.0 ng/m³ (9.8 ppt), Kansas 1972. The means of the positive samples were 15.9 ng/m³ (1.5 ppt) for

1970, 3.8 ng/m^3 (0.4 ppt) for 1971, and 11.6 ng/m^3 (1.1 ppt) for 1972. Yearly means of all samples (non-detect and trace values treated as zero) were 1.2 ng/m^3 (0.1 ppt) in 1970, 0.2 ng/m^3 (0.02 ppt) in 1971, and 1.6 ng/m^3 (0.2 ppt) in 1972.

Kutz (1983) reported results for ambient methyl parathion monitoring at ten locations in eight states, including two urban sites in California (Pasadena and Fresno). Other sample sites were located in Alabama, Illinois, Mississippi, Montana, South Carolina, and Texas. Analytical procedures performed by Kutz (1983) tested for the presence of p–nitrophenol, a breakdown product of both ethyl and methyl parathion. The maximum p–nitrophenol concentration equated to 160 ng/m^3 (14.88 ppt), and the arithmetic mean for all samples was 2.9 ng/m^3 (0.27 ppt). No information was presented concerning the analytical or sampling methodology, nor was the mean of the positive detections presented.

Arthur *et al.* (1976) conducted air monitoring for methyl parathion over a three-year period (1972 to 1974) at Stoneville, Mississippi. This site was located in the middle of the most intensive cotton-growing area of Mississippi and it was the same site monitored by Stanley *et al.* (1971). Samples were collected for 4.3 minutes each hour (12 hours/week) over the week-long sampling period, representing a volume of approximately 7.0 m^3 of air/sample. Results were averaged on a monthly basis and a summary of these values is presented in Table 8. There were 156 total weekly samples taken with a maximum reported methyl parathion concentration of 2,060 ng/m^3 (191.6 ppt) and the highest ambient concentration for methyl parathion reported in the literature. Methyl parathion was detected in samples taken from 5 months in 1972, 6 months in 1973, and 10 months in 1974. Concentrations of methyl parathion never exceeded 1 ng/m^3 from November through May, but increased in June and July, and peaked in August or September. Peak concentrations, were 216.9 ng/m^3 (20.2 ppt) in August 1972, 791.1 ng/m^3 (73.6 ppt) in September 1973, and 341.1 ng/m^3 (31.72ppt) in August 1974.

Sava (1985) measured the concentrations of agricultural chemicals present in air at residences located near agricultural lands in Salinas, California. Consecutive six-hour air samples were collected over a four-day period at three residential sites adjacent to agricultural fields. Methyl parathion was detected at 17 ng/m^3 (1.6 ppt) in a single sample collected at a site 1,200 feet downwind from the nearest agricultural field.

4.7. Conclusions

In summary, airborne concentrations of methyl parathion are dependent on both the intrinsic properties of the chemical as well as environmental factors. Methyl parathion's presence in air may be attributed to drift from direct aerial application of the pesticide, volatilization from soil and foliar surfaces and to a lesser extent volatilization from field-waters. Due to methyl parathion's comparatively low Henry's Law constant and volatility, the total volatile flux from this last environmental component is low (Benson and Long; 1991; Dortland, 1980; Dowling and Lemley; 1995; Kadlec and Benson; 1995; Kamiya et al; 1995; Kamiya et al. 1992; Lassiter *et al.* 1986; McChesney and Seiber, 1986; Newton et al. 1990; Seiber *et al.*, 1989).

The major route of methyl parathion degradation in soil and water appears to be microbially mediated. Although under some soil conditions (temperature . 6 °C) the half–life of methyl parathion may be as long as 40 days, under representative field conditions methyl parathion is rapidly degraded in soil (half–life 0.75 – 2-3 days). The major route of methyl parathion degradation on plant surfaces appears to be controlled by sunlight on foliar surfaces. The half–life ranges from 1.6 – 38 hours. Since methyl parathion is rapidly degraded in soil and on foliar surfaces, volatilization after application should play a lesser role in the atmospheric loading of methyl parathion than will drift and volatilization occurring at the time of application (McChesney and Seiber, 1986; Seiber et al. 1989).

From literature sources, the maximum concentrations of methyl parathion in ambient air ranged from 5 ng/m^3 (0.5 ppt) to 191.58 ng/m^3 (19.0 ppt): Concentrations of methyl parathion measured during and following application ranged from 512 ng/m^3 (sampler placed 17 meters from field) (ARB, 1989) to 7,400 ng/m^3 have been reported in air samples collected at sites of application (in field and 1 meter away) (Jackson and Lewis, 1979). Although the fate of atmospheric methyl parathion has not been extensively studied, its presence in air (following application) has been shown to decrease rapidly to background concentrations over a period of from 1–3 days after application (ARB, 1989; Jackson and Lewis, 1979; Seiber and McChesney, 1987; Stanley *et al.*, 1971).

4.8. References

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5. AIRBORNE CONCENTRATIONS OF METHYL PARATHION IN CALIFORNIA.

5.1. Introduction

As required by AB 1807, (Section 14022(c), Article 1.5, Food and Agricultural Code) DPR requests ARB to document the airborne concentrations of pesticides, in this case, methyl parathion. Two studies were conducted. The University of California, Davis, performed the first study, Ambient Air Monitoring of Methyl Parathion. In this study, the levels of airborne emissions of methyl parathion in ambient air were measured in Colusa and Sutter Counties during the season of use (May 12–June 12) in 1986. The second study, *Off-Site Air Monitoring of Methyl Parathion*, was performed by the ARB. In this study, the levels of airborne emissions of methyl parathion were measured before, during, and after an application.

5.2. Ambient Air Monitoring of Methyl Parathion

5.2.1. Abstract

Personnel from the Department of Environmental Toxicology at the University of California, Davis, measured airborne levels of methyl parathion. Air samples were collected for 24-hour intervals at monitoring sites in the towns of Trowbridge and Robbins in Sutter County and Maxwell and Williams in Colusa County. Sampling for background concentrations of methyl parathion was conducted in Davis, Yolo County. Air samples were collected from May 12 to June 12, 1986, corresponding with the season during which methyl parathion had been historically applied to rice fields in these counties. Additionally, samples of 3-hour duration were collected every Monday at Maxwell to quantify peak values. All samples were analyzed for methyl parathion and its major transformation product, methyl paraoxon. The amount of methyl parathion applied to all townships (ideally a six mile by six mile square) adjacent to the location of the sampling sites during the sampling period, was 11,584 lbs AI for the Maxwell/Williams area and 2,207 lbs AI for the Trowbridge/Williams). There was one application of methyl parathion, 8.0 lbs AI, in a township adjacent to where the background sample was collected at Davis.

Airborne concentrations of methyl parathion were detected at all sampling sites. Average concentrations (based on $\log_n$ transformation of the data) for Trowbridge were 0.7 ng/m^3 (0.07 ppt) with 23% of the samples testing positive, and for Robbins were 0.5 ng/m^3 (0.05 ppt) with 27% testing positive. Average methyl parathion concentrations were 5.0 ng/m^3 (0.47 ppt)—70 % of samples testing positive at Maxwell, and 2.3 ng/m^3 (0.2 ppt)—69% testing positive for samples collected at Williams. A single positive sample of 0.4 ng/m^3 (0.04 ppt) was collected at the background sampler located in Davis.

Methyl paraoxon was detected at the Maxwell and Williams but was not detected in samples collected at either Trowbridge or Robbins, or at the background station at Davis. The means for 24-hour methyl paraoxon samples for Maxwell were 1.8 ng/m^3 (0.17 ppt) and for Williams were 0.9 ng/m^3 (0.08 ppt).

Two of the fourteen 3-hour samples, collected at Maxwell, tested positive for methyl parathion and/or methyl paraoxon. The highest 3-hour sample concentration of methyl parathion was 8.9 ng/m^3 (0.8 ppt) and of methyl paraoxon, 4.6 ng/m^3 (0.4 ppt). Mean concentrations averaged 6.0 ng/m^3 (0.6 ppt) and 3.1 ng/m^3 (0.3 ppt), respectively.

The highest 24-hour concentration of methyl parathion plus methyl paraoxon converted to methyl parathion equivalents ([MP+MPEV]) was found at Maxwell on May 13, 1986 and consisted of 28.1 ng/m^3 (2.6 ppt). The mean [MP+MPEV] at this site throughout the study period was 11.5 ng/m^3 (1.1 ppt). At Williams, the mean [MP+MPEV] concentration was 6.0 ng/m^3 (0.6 ppt), approximately one-half the mean concentration measured at Maxwell. The [MP+MPEV] means for the samples taken from Trowbridge or Robbins were 0.4 ng/m^3 (.04 ppt).

5.2.2. Introduction

On February 13, 1985, DPR requested ARB to monitor airborne levels of methyl parathion. A monitoring recommendation, which included information about methyl parathion's chemical and physical characteristics, target pests, and historical use patterns, was sent to ARB on December 24, 1985, to assist them in selecting sampling sites.

It was recommended that monitoring for ambient air concentrations of methyl parathion be conducted during the month of May and/or June. This period for sampling corresponded with historical use patterns of methyl parathion to flooded rice fields for the control of tadpole shrimp. Colusa and Sutter counties were recommended as the best locations for such monitoring. Subsequent to this recommendation, the ARB contracted with the Department of Environmental Toxicology at the University of California, Davis, to conduct the study. A summary of their study follows.

5.2.3. *Materials and Methods*

5.2.3.1. Sites

Monitoring sites in Sutter County were East Nicolaus High School in Trowbridge and Robbins Elementary School in Robbins. Monitoring sites in Colusa County were Maxwell High School and Williams City Hall. Monitoring was conducted in these areas because of their locations within regions of high methyl parathion use. Considerations of safety and security, permission to use the site, and availability of electrical power were factors contributing to the exact placement of air samplers. Background sampling was performed on the University of California, Davis campus in Yolo County, a site where methyl parathion was not historically applied. High volume air samplers were co-located (two each per site) at Trowbridge, Robbins, Williams and Davis, while three co-located air samplers were placed at Maxwell. The air samplers at Trowbridge, Robbins, and Maxwell were located within 0.5 miles of rice fields. The sample site at Williams was within the city limits, approximately a mile in all directions from the nearest rice fields. All air samplers were positioned in accordance with the criteria outlined in the U.S. USEPA Ambient Air Quality Monitoring, Data Reporting, and Surveillance Provisions, Title 40, Code of Federal Regulations (CFR), section 58, Ambient Air Quality Surveillance, Appendix E, Probe Siting Criteria For Ambient Air Quality Monitoring.

5.2.3.2. Sampling

High volume air sampler pumps were modified with a 3 to 5 port manifold to allow an airflow of approximately 50 liters per minute (lpm). In-line flow meters were installed, and flow rates were recorded at the beginning and end of each sampling period. Air samplers were connected with Tygon tubing to Teflon sampler cups containing XAD-4 resin adsorbent. The sampler cups were covered with glass wool and capped to prevent the entrance of sunlight.

Cups were placed approximately two meters apart, and 1.67 meters above the rooflines of structures on which they were placed. Samplers were operated for 24-hour periods, and were collected Tuesday through Friday at Maxwell and Monday through Friday (four 24–hour periods per week) at all other sampling stations. On Mondays at Maxwell, two to four 3-hour samples were collected followed by a single sample of 18 to 12 hours duration. All samples were transported from the field to the laboratory on dry ice and stored at -20 °C until analyzed. Samples were analyzed for the presence of methyl parathion and/or methyl paraoxon within one month of sample collection.

Flow rates ranged from 40 to 60 lpm depending on the number of samplers and in-line rotometers. Airflows were measured at the start and end of each sampling period via attaching a flow meter to the entrance of the sampling cups. To convert airflows to lpm each flow meter reading was multiplied by the calibration equation (0.85 x flow meter reading minus 1.2). Total sample volume was determined by taking the average of the two airflows as calculated above.

5.2.3.3. Extraction.

Samples were extracted by first washing them with 90-150 ml of ethyl acetate for 30 minutes, after which the solvent was decanted and filtered through Whatman #1 filter paper. The eluant was saved and the XAD-4 resin was washed again with fresh solvent for 15 minutes, then decanted and filtered, and the eluant combined with the above. A final washing was then performed for 10 minutes, and the eluant treated as above. Combined eluants were concentrated on a steam bath to approximately 6 ml.

5.2.3.4. Analysis.

Methyl parathion and methyl paraoxon were analyzed on a Hewlett Packard 5710A gas chromatograph with a nitrogen-phosphorous detector. A Tracor MT-220 with a flame photometric detector was also used for analysis if there were interfering, compounds present, or to confirm positive results in samples near the limit of detection.

Injecting various volumes of a standard methyl parathion or methyl paraoxon solution created a four or five point standard curve. For analysis, each sample was injected twice, and the average of the two areas was then used to calculate the concentration of methyl parathion or paraoxon. Standards were injected after every two samples. Analyses were considered valid if the standard agreed within three percent of the original standard curve. Recovery studies (methods below) were performed prior to sample extraction. The minimum detection limit (MDL) for methyl parathion was 0.2 ng/m^3 (0.02 ppt) and 0.5 ng/m^3 (0.05 ppt) for methyl paraoxon.

5.2.3.5. Recovery and Trapping Efficiency.

Recovery from XAD resin spiked with 0.1 or 2.0 μg of methyl parathion was 99.5% (111% and 87%) and 98%, respectively (Appendix 2) Recovery from XAD resin spiked with 0.1 μg methyl paraoxon was 87%. XAD resin was also spiked with methyl parathion and methyl paraoxon, and then placed in a freezer at -20 °C for 11 weeks. Recoveries were 86% and 67%, respectively.

Trapping efficiency was determined as follows: Sample cups were connected to air samplers operating under conditions similar to those in the field. Glass wool was spiked with methyl parathion and placed upstream of the sample cups. A second sample cup was attached to check for breakthrough. Air was drawn through the sample cups at 50 lpm for 22 to 24 hours. The percent recovery was 85% and 82% respectively. Neither methyl parathion nor methyl paraoxon was detected in the breakthrough cups.

Calculations of precision for the co-located samplers were carried out using the equation described in the U.S. USEPA guidelines, Title 40, Code of the Federal Regulations, section 58. Precision for all samples positive for methyl parathion ranged from -22.3% to 20.7% at all sites.

5.2.3.6. Use Reports.

Methyl parathion use information was obtained from the 1986 Pesticide Use Report database for the period May 1 through June 12, 1986, for those townships adjacent to sampling sites in Colusa, Sutter, and Yolo counties. This information is presented in Table 9. Methyl parathion was applied 236 times in the Maxwell and Williams area, and approximately 11,616.6 lbs AI were applied to 18,548.0 acres (Table 9). From May 10 to May 21, 1986, 8,972.6 lbs AI of methyl parathion were applied in 178 applications to 13,367.6 acres. These applications account for 75 percent of methyl parathion's use in townships adjacent to sampling, during the sampling period.

TABLE 9.

METHYL PARATHION APPLICATIONS IN TOWNSHIPS ADJACENT TO MONITORING STATIONS FOR MAY/JUNE 1986[a]

Date	MAXWELL/WILLIAMS Number of Applications	Acres Treated	Pounds	TROWBRIDGE/ROBBINS Number of Applications	Acres Treated	Pounds
MAY						
2	—[b]	—	—	1	134.4	32.3
3	—	—	—	—	—	—
4	2	205.5	136.4	—	—	—
5	3	125.5	98.6	—	—	—
6	10	540.4	363.1	—	—	—
7	3	347.8	227.9	—	—	—
8	—	—	—	—	—	—
9	—	—	—	—	—	—
10	20	1,285.4	817.9	—	—	—
11	3	151.2	98.6	—	—	—
12[c,d]	1	98.8	70.7	—	—	—
13	24	1,656.9	1,173.7	—	—	—
14	13	948.5	610.8	—	—	—
15	26	3,081.6	1,432.7	—	—	—
16	6	202.5	139.5	—	—	—
17	12	1,290.3	908.8	—	—	—
18	16	1,272.5	924.0	2	199.6	135.5
19[d]	13	1,545.7	1,001.1	2	492.0	448.4
20	22	1,355.5	840.2	1	104.2	51.7
21	17	1,344.4	867.2	—	—	—
22	6	406.1	251.7	1	205.5	103.4
23	9	684.7	448.2	3	330.0	166.6
24	1	79.0	50.6	3	400.1	321.6
25	0	—	—	—	—	—
26	3	209.5	143.0	2	332.0	250.6
27[d]	0	0.0	0.0	4	655.0	468.3
28	2	286.5	187.0	2	203.5	194.5
29	10	864.5	455.0	—	—	—
30	5	143.3	89.1	—	—	—
31	1	144.2	92.2	—	—	—
JUNE						
1	1	19.8	10.2	—	—	—
02[d]	1	93.9	59.9	—	—	—
3	0	0	0	—	—	—
4	3	150.2	106.1	—	—	—
5	1	13.8	12.6	—	—	—
09[d]	0	0	0	—	—	—
12	0	0	0	1	34.6	33.6
TOTALS	236	18,548.0	11,616.6	22	3,091.0	2,206.5

a/ Areas consist of the township/range in which the sampler was located extended by a township in all directions. Information was obtained from the 1986 Pesticide Use Report .

b/ — indicates that no application of methyl parathion ocurred.

c/ First sampling date.

d/ Dates on which 3-hour samples were taken.

In contrast, fewer applications of methyl parathion were made to fields near the sampling sites at Trowbridge and Robbins (Table 9). From May 1 through June 12, approximately 2,206 lbs of methyl parathion were applied to 3,092 acres in 22 applications. One application of methyl parathion occurred on May 2, 1986, and there were no applications of methyl parathion from May 3, through May 17, 1986. Methyl parathion was applied on May 18, May 19, May 20, May 22, May 24, and from May 26 to May 28. One final application was made on June 12, 1986 (Table 9).

5.2.3.7. Statistical Analysis

The average of the air concentrations from the co-located samplers for each day at each site was calculated via a log-n transformation of the data. This value was then used to calculate the average concentration (mean + standard deviation) of methyl parathion present at that site for the duration of the study. If a sample from one of the co-located samplers was lost or observed to be below the analytical detection limit, the remaining positive result was used as the value for that day at that site. Means and standard deviations were calculated for all positive values, for methyl parathion and paraoxon both 3-hour and 24-hour samples. An arithmetic mean was calculated for the 24-hour sample periods using all values. In calculating the arithmetic mean, all-non–detects were assigned the MDL value.

5.2.4. Results

5.2.4.1. 24-hour Samples

Methyl parathion results for 24-hour air sampling are expressed in ng/m^3 (Table 10a) and in ppt (Table 10b). The majority of positive samples for all sample sites were collected between May 13-30.

At Trowbridge, 23% (10 of 44) samples were positive for methyl parathion, with the remaining 77% (34 of 44) below the MDL. Values for positive samples ranged from 0.5 ng/m^3 to 1.1 ng/m^3 (0.05 ppt to 0.10 ppt). The mean was 0.4 ng/m^3 (0.04 ppt) for Trowbridge, calculated using the average values for the 15 days between May 12 and May 30. Values for positive samples collected at Robbins ranged from 0.3 ng/m^3 to 0.7 ng/m^3 (0.03 ppt to 0.07 ppt) with 27% (10 of 37 samples) testing positive for methyl parathion. The mean for Robbins (using the 10 positive samples) was 0.4 ng/m^3 (0.04 ppt).

TABLE 10a. AMBIENT AIR CONCENTRATIONS OF METHYL PARATHION (ng/m^3)[a]

DATE	SUTTER COUNTY				COLUSA COUNTY				
	TROWBRIDGE		ROBBINS		MAXWELL			WILLIAMS	
	A[b]	B	A	B	A	B	C	A	B
12–May[c]	0.6	0.5	0.7	0.7	4.5	7.0	8.5	0.7	1.3
13–May	1.0	1.1	0.6	0.4	22.2	24.7	30.1	3.9	5.5
14–May	0.5	0.6	0.6	0.5	20.1	21.3	23.2	22.8	20.7
15–May	—[d]	—	0.3	0.4	12.4	14.1	14.9	5.4	5.7
19–May[c]	—	—	—	—	14.5	15.2	15.0	5.3	5.3
20–May	—	—	—	NS[e]	5.5	5.5	4.0	5.7	4.8
21–May	1.0	1.1	0.4	—	15.5	12.0	14.4	4.8	4.7
22–May	—	—	0.5	—	8.6	6.8	7.8	1.5	1.4
27–May[c]	—	—	NS	NS	2.4	2.4	1.7	1.2	1.5
28–May	—	—	—	—	4.7	5.0	7.5	1.6	2.0
29–May	—	—	—	—	3.0	2.8	2.8	NS	NS
30–May	—	—	—	—	1.3	1.8	1.6	NS	NS
2–June[c]	—	—	—	—	—	—	—	—	—
3–June	—	—	—	—	—	—	—	—	—
4–June	—	—	—	—	—	—	—	—	—
5–June	—	—	—	—	—	—	—	—	—
9–June[c]	—	—	—	—	—	—	—	—	—
10–June	—	—	—	—	—	—	0.5	—	0.6
11–June	NS	NS	—	—	0.7	0.7	0.7	0.7	0.6
12–June	0.5	0.5	—	—	—	0.4	0.3	0.3	0.3
	All[f]	P	All	P	All	P		All	P
n	38	10	37	10	60	42		36	25
mean	0.2	0.8	0.1	0.5	6.2	8.8		3.0	4.3
SD	0.4	0.3	0.2	0.1	7.7	7.8		5.0	5.5
%Positive	26%		27%		70%			69%	

a/ A single sample collected at the University of California, Davis campus, tested positive for methyl parathion at a concentration of 0.04 ng/m^3.

b/ A,B or A, B, C indicate co-located samplers at the collection sites.

c/ Dates when 3-hour samples were collected at Maxwell. Values listed represent the sum of values from three hour sample plus values from samples collected for the remainder of the day.

d/ "—" indicates sample concentrations below the minimum detection level 0.2 ng/m^3.

e/ "NS" indicates days when no samples were taken.

f/ "P" = positive samples, All = all samples.

TABLE 10b. AMBIENT AIR CONCENTRATIONS OF METHYL PARATHION (ppt)[a]

DATE	SUTTER COUNTY				COLUSA COUNTY				
	TROWBRIDGE		ROBBINS		MAXWELL			WILLIAMS	
	A[b]	B	A	B	A	B	C	A	B
12–May[c]	0.1	0.1	0.1	0.1	0.4	0.7	0.8	0.1	0.1
13–May	0.1	0.1	0.1	0.0	2.1	2.3	2.8	0.4	0.5
14–May	0.1	0.1	0.1	0.1	1.9	2.0	2.2	2.1	1.9
15–May	—[d]	—	0.0	0.0	1.2	1.3	1.6	0.5	0.5
19–May[c]	—	—	—	—	1.3	1.4	1.4	0.5	0.5
20–May	—	—	—	NS[e]	0.5	0.5	0.4	0.5	0.5
21–May	0.1	0.1	0.0	—	1.4	1.1	1.3	0.5	0.4
22–May	—	—	0.1	—	0.8	0.6	0.7	0.1	0.1
27–May[c]	—	—	NS	NS	0.2	0.2	0.2	0.1	0.1
28–May	—	—	—	—	0.4	0.5	0.7	0.2	0.2
29–May	—	—	—	—	0.3	0.3	0.3	NS	NS
30–May	—	—	—	—	0.1	0.2	0.2	NS	NS
2–June[c]	—	—	—	—	—	—	—	—	—
3–June	—	—	—	—	—	—	—	—	—
4–June	—	—	—	—	—	—	—	—	—
5–June	—	—	—	—	—	—	—	—	—
9–June[c]	—	—	—	—	—	—	—	—	—
10–June	—	—	—	—	—	—	0.05	—	0.06
11–June	NS	NS	—	—	0.7	0.7	0.07	0.07	0.06
12–June	0.05	0.05	—	—	—	0.04	0.03	0.03	0.03
	All[f]	P	All	P	All	P		All	P
n	38	10	37	10	60	42		36	25
mean	0.02	0.07	0.01	0.05	0.58	0.82		0.28	0.40
SD	0.04	0.03	0.02	0.01	0.72	0.73		0.47	0.51
%Positive	26%		27%		70%			69%	

a/ A single sample collected at the University of California, Davis campus, tested positive for methyl parathion at a concentration of 0.04 ppt.

b/ A, B or A, B, C indicates co-located samplers at the collection sites.

c/ Dates when 3-hour samples were collected at Maxwell. Values listed represent the sum of values from three hour sample plus values from samples collected for the remainder of the day.

d/ "—" indicates sample concentrations below the minimum detection level 0.02 ppt.

e/ "NS" indicates days when no samples were taken.

f/ "P" = positive samples, All = all samples.

At Maxwell, 70% (42 of 60) of the samples were positive for methyl parathion with values ranging from 0.3 ng/m^3 to 30.1 ng/m^3 (0.03 ppt to 2.80 ppt). The mean for Maxwell was 10.6 ng/m^3 (0.99 ppt) for 12 sample sets from May 12, to May 30, 1986. At Williams, 69% (25 of 36) of the samples were positive for methyl parathion, with the values ranging from 0.3 ng/m^3 to 22.8 ng/m^3 (0.03 ppt to 2.12 ppt). The mean at Williams was 5.1 ng/m^3 (0.47 ppt), calculated for ten positive samples. A single sample out of 30 samples taken at the background site (Davis) tested positive 0.4 ng/m^3 (0.04 ppt) for methyl parathion.

Methyl paraoxon was not detected in samples collected at Trowbridge, Robbins, or Davis. Methyl paraoxon was detected in 24-hour samples collected at Maxwell/Williams with results expressed in ng/m^3 (Tables 11 a) and ppt (Table 11b). Methyl paraoxon was detected in 41% (24 of 59) of samples collected at Maxwell, and 42% (15 of 36) of samples collected at Williams. Concentrations ranged from 0.5 to 7.8 ng/m^3 (0.05 ppt to 0.73 ppt) at Maxwell and from 0.5 to 1.4 ng/m^3 (0.05 ppt to 0.13 ppt) at Williams. The site means were 1.8 ng/m^3 (0.17 ppt) for samples collected at Maxwell and 0.9 ng/m^3 (0.08 ppt) at Williams.

5.2.4.2. 3-hour Samples

A total of forty-two 3-hour samples were collected at Maxwell on May 12, 19, 27, June 2, and June 9, 1986. Methyl parathion and methyl paraoxon were detected in five of 6 samples collected on May 19 (Table 12), during the two 3-hour intervals from 8 a.m. to 11 a.m. and 11 a.m. to 2 p.m.. In these samples, the concentration of methyl parathion ranged from 2.6 ng/m^3 to 8.9 ng/m^3 (0.24 ppt to 0.83 ppt); the mean of these samples was 6.0 ng/m^3 (0.56 ppt). Three of these five samples (Table 13) also tested positive for methyl paraoxon.

Methyl paraoxon concentrations ranged from 2.2 ng/m^3 to 4.6 ng/m^3 (0.2 ppt to 0.4 ppt); the mean for these samples was 3.1 ng/m^3 (0.3 ppt). The average concentration of methyl paraoxon was only 52% of the concentration of methyl parathion in 3-hour samples. Neither methyl parathion nor methyl paraoxon were detected in 3-hour samples collected on the other sampling dates.

TABLE 11a. AMBIENT AIR CONCENTRATIONS OF METHYL PARAOXON (ng/m^3)[a]

DATE	SUTTER COUNTY				COLUSA COUNTY				
	TROWBRIDGE		ROBBINS		MAXWELL			WILLIAMS	
	A[b]	B	A	B	A	B	C	A	B
12–May[c]	—[d]	—	—	—	—	—	—	—	—
13–May	—	—	—	—	1.8	2.5	2.7	0.9	1.4
14–May	—	—	—	—	0.5	0.9	1.1	1.0	0.5
15–May	—	—	—	—	7.8	—	6.9	0.5	1.2
19–May[c]	—	—	—	—	1.4	0.5	2.0	—	0.8
20–May	—	—	—	NS[e]	0.7	0.8	0.5	0.9	1.0
21–May	—	—	—	—	1.9	—	2.4	1.0	1.0
22–May	—	—	—	—	3.0	2.3	3.9	—	1.0
27–May[c]	—	—	NS	NS	—	—	—	0.7	—
28–May	—	—	—	—	1.7	1.8	NS	0.6	0.8
29–May	—	—	—	—	0.6	0.7	0.6	NS	NS
30–May	—	—	—	—	—	—	0.9	NS	NS
2–June[c]	—	—	—	—	—	—	—	—	—
3–June	—	—	—	—	—	—	—	—	—
4–June	—	—	—	—	—	—	—	—	—
5–June	—	—	—	—	—	—	—	—	—
9–June[c]	—	—	—	—	—	—	—	—	—
10–June	—	—	—	—	—	—	—	—	—
11–June	NS	NS	—	—	—	—	—	—	—
12–June	—	—	—	—	—	—	—	—	—
	P	All	P	All	P		All	P	All
n	0	38	0	37	25		59	15	36
mean	NS		NS		2.0		1.1	0.90	0.70
SD	NS		NS		1.8		1.4	0.24	0.27
%Positive	0%		0%		42%			42%	

a/ No samples collected at the University of California, Davis campus, tested positive for methyl paraoxon.

b/ A,B or A, B, C indicate co-located samplers at the collection sites.

c/ Dates when 3-hourr samples were collected at Maxwell. Values listed represent the sum of values from three hour sample plus values from samples collected for the remainder of the day.

d/ "—" indicates sample concentrations below the minimum detection level 0.5 ng/m^3.

e/ "NS" indicates days when no samples were taken.

f/ "P" = positive samples, All = all samples.

TABLE 11b. AMBIENT AIR CONCENTRATIONS OF METHYL PARAOXON (ppt)[a]

DATE	SUTTER COUNTY TROWBRIDGE A[b]	SUTTER COUNTY TROWBRIDGE B	SUTTER COUNTY ROBBINS A	SUTTER COUNTY ROBBINS B	COLUSA COUNTY MAXWELL A	COLUSA COUNTY MAXWELL B	COLUSA COUNTY MAXWELL C	COLUSA COUNTY WILLIAMS A	COLUSA COUNTY WILLIAMS B
12–May[c]	—[d]	—	—	—	—	—	—	—	—
13–May	—	—	—	—	0.17	0.22	0.23	0.08	0.13
14–May	—	—	—	—	0.05	0.07	0.1	0.09	0.05
15–May	—	—	—	—	0.73	—	0.64	0.05	0.11
19–May[c]	—	—	—	—	0.13	0.05	0.18	—	0.08
20–May	—	—	—	NS[e]	0.07	0.07	0.05	0.08	0.09
21–May	—	—	—	—	0.18	—	0.22	0.09	0.09
22–May	—	—	—	—	0.28	0.21	0.36	—	0.09
27–May[c]	—	—	NS	NS	—	—	—	0.07	—
28–May	—	—	—	—	0.16	0.17	NS	0.06	0.07
29–May	—	—	—	—	0.06	0.07	0.06	NS	NS
30–May	—	—	—	—	—	—	0.08	NS	NS
2–June[c]	—	—	—	—	—	—	—	—	—
3–June	—	—	—	—	—	—	—	—	—
4–June	—	—	—	—	—	—	—	—	—
5–June	—	—	—	—	—	—	—	—	—
9–June[c]	—	—	—	—	—	—	—	—	—
10–June	—	—	—	—	—	—	—	—	—
11–June	NS	NS	—	—	—	—	—	—	—
12–June	—	—	—	—	—	—	—	—	—
	P	All[f]	P	All	P		All	P	All
n	0	38	0	37	25		59	15	36
mean	NS		NS		0.19		0.1	0.08	0.09
SD	NS		NS		0.17		0.13	0.01	0.02
%Positive	0%		0%			42%		42%	

a/ No samples collected at the University of California, Davis campus, tested positive for methyl paraoxon.

b/ A,B or A, B, C indicate co-located samplers at the collection sites.

c/ Dates when 3-hour samples were collected at Maxwell. Values listed represent the sum of values from three hour sample plus values from samples collected for the remainder of the day.

d/ "—" indicates sample concentrations below the minimum detection level 0.05 ppt.

e/ "NS" indicates days when no samples were taken.

f/ "P" = positive samples, All = all samples.

TABLE 12. CONCENTRATIONS OF METHYL PARATHION IN 3-HOUR AIR SAMPLES COLLECTED AT MAXWELL

SAMPLE		ng/m³			ppt		
DATE	TIME	A[a]	B	C	A	B	C
12-May	8:30	—[b]	—	—	—	—	—
12-May	11:30	—	—	—	—	—	—
12-May	14:30	—	—	—	—	—	—
19-May	8:10	6.4[c]	8.9	7.4	0.60	0.83	0.69
19-May	11:05	2.6	4.7	—	0.25	0.44	—
27-May	8:02	—	—	—	—	—	—
27-May	11:00	—	—	—	—	—	—
27-May	13:50	—	—	—	—	—	—
27-May	16:35	—	—	—	—	—	—
2-June	8:00	—	—	—	—	—	—
2-June	11:05	—	—	—	—	—	—
9-June	8:05	—	—	—	—	—	—
9-June	11:00	—	—	—	—	—	—
9-June	14:15	—	—	—	—	—	—

a/ A, B, C are co-located samplers.
b/ Mean of positive samples equals 6.0 ng/m³, or 0.56 ppt.
c/ "—" Indicates sample values below the MDL of 0.9 ng/m³, or 0.08 ppt.

TABLE 13. CONCENTRATIONS OF METHYL PARAOXON IN 3-HOUR AIR SAMPLES COLLECTED AT MAXWELL

SAMPLE		ng/m³			ppt		
DATE	TIME	A[a]	B	C	A	B	C
19-May	8:10	4.6[b]	—[c]	2.2	0.43	—	0.2
19-May	11:05	—	2.6	—	—	0.24	—

a/ A, B, C are co-located samplers.
b/ Mean of positive samples equals 3.1 ng/m³, or 0.29 ppt.
c/ "—" indicates sample values below the MDL of 2.0 ng/m³, or 0.19 ppt.

5.2.4.3. *Total Residue*

Ambient air concentrations of the total residue were calculated, and are presented in ng/m^3 (Table 14a) and in ppt (Table 14b). Methyl paraoxon values were converted to methyl parathion equivalent values (MPEV) by multiplying the measured paraoxon values by 1.06 (see Appendix 1). The MPEVs were then added to the measured methyl parathion levels (Table 10a, 10b) for a given sample and the resultant sum represents the adjusted total ambient air concentration of methyl parathion residue. Samples in which methyl paraoxon concentrations were below the MDL were assumed to contain no methyl paraoxon. Methyl parathion total residues are not presented for dates on which methyl parathion or methyl paraoxon were not detected.

When there was a measurable amount of methyl parathion but not a measurable amount of methyl paraoxon in a sample, it was not possible to identify that particular sample's methyl parathion total residue. However, the mean total methyl parathion total residue for each site was estimated as the mean of a weighted sum:

$$\text{MEAN total methyl parathion} = \frac{\text{MEAN [methyl parathion]} + (1.06 \times \text{MEAN]methyl paraoxon]})}{\text{TOTAL RESIDUE}}.$$

A summary of methyl parathion total residue is presented as Table 15. Average values for methyl parathion total residue values were calculated for Maxwell and Williams but not for the other sample locations The mean total residue value for Maxwell was 13.0 ng/m^3 (1.2 ppt), and the mean total residue for Williams was 6.7 ng/m^3 (0.6 ppt) (Table 15). The highest average total residue value for 24-hour samples was 27.8 ng/m^3 (2.6 ppt) for Maxwell on May 13, 1986 (Table 15). The highest 24-hour total residue value from Williams was 22.6 ng/m^3 (2.10 ppt). The mean total residue for Maxwell and Williams was 9.9 ng/m^3 (0.9 ppt). Total residue values were not calculated for Trowbridge, Robbins, or Davis, because methyl paraoxon was not detected in samples collected at these sites.

TABLE 14a. AIR CONCENTRATIONS OF METHYL PARATHION TOTAL RESIDUE (ng/m³)[a]

DATE	SUTTER COUNTY TROWBRIDGE A[b]	SUTTER COUNTY TROWBRIDGE B	SUTTER COUNTY ROBBINS A	SUTTER COUNTY ROBBINS B	COLUSA COUNTY MAXWELL A	COLUSA COUNTY MAXWELL B	COLUSA COUNTY MAXWELL C	COLUSA COUNTY WILLIAMS A	COLUSA COUNTY WILLIAMS B
12-May[c]	0.6	0.5	0.7	0.7	4.5	7.0	8.5	0.7	1.3
13-May	1.0	1.1	0.6	0.4	23.1	27.4	33	4.9	7
14-May	0.5	0.6	0.5	0.5	20.6	22.3	24.4	23.9	21.2
15-May	—	—	0.3	0.4	20.7	14.1	21	5.9	7
19-May[c]	—	—	—	—	16.0	15.7	17.1	5.3	6.2
20-May	—	—	—	NS[e]	6.2	6.4	4.5	6.7	5.9
21-May	1.1	1.1	0.4	—	17.5	12	16.9	5.9	5.8
22-May	—	—	0.5	—	11.8	9.2	11.9	1.5	2.1
27-May[c]	—	—	NS	NS	2.4	2.4	1.7	2	1.5
28-May	—	—	—	—	6.5	6.9	7.5	3.2	2.9
29-May	—	—	—	—	3.6	3.3	3.5	NS	NS
30-May	—	—	—	—	1.3	1.8	2.5	NS	NS
2-June[c]	—	—	—	—	—	—	—	—	—
3-June	—	—	—	—	—	—	—	—	—
4-June	—	—	—	—	—	—	—	—	—
5-June	—	—	—	—	—	—	—	—	—
9-June[c]	—	—	—	—	—	—	—	—	—
10-June	—	—	—	—	—	—	0.5	—	0.6
11-June	NS	NS	—	—	0.7	0.7	0.7	0.7	0.6
12-June	0.5	0.5	—	—	—	0.4	0.3	0.3	0.3

a/ One sample collected at the University of California, Davis campus, tested positive for methyl parathion. No samples at UC Davis tested positive for methyl paraoxon.

b/ A, B or A, B, C indicate co-located samplers at the collection sites.

c/ Dates when 3-hour samples were collected at Maxwell. Values listed represent the sum of values from three hour sample plus values from samples collected for the remainder of the day.

d/ "—" indicates sample concentration below the minimum detection level, of 0.02 ppt for methyl parathion and 0.05 ppt for methyl paraoxon respectively.

e/ "NS" indicates days where no samples were taken.

TABLE 14b. AIR CONCENTRATIONS OF METHYL PARATHION TOTAL RESIDUE (ppt)[a]

DATE	SUTTER COUNTY				COLUSA COUNTY				
	TROWBRIDGE		ROBBINS		MAXWELL			WILLIAMS	
	A[b]	B	A	B	A	B	C	A	B
12-May[c]	0.06	0.05	0.06	0.06	0.42	0.65	0.8	0.06	0.12
13-May	0.09	0.1	0.06	0.04	2.23	2.52	3.03	0.45	0.64
14-May	0.05	0.06	0.05	0.05	1.93	2.05	2.26	2.17	1.97
15-May	—	—	0.06	0.04	1.88	1.31	2.23	0.55	0.66
19-May[c]	—	—	—	—	1.46	1.46	1.57	0.49	0.57
20-May	—	—	—	NS[e]	0.58	0.59	0.43	0.61	0.54
21-May	0.1	0.1	0.04	—	1.61	1.11	1.55	0.54	0.53
22-May	—	—	0.05	—	1.08	0.84	1.29	0.14	0.22
27-May[c]	—	—	NS	NS	0.23	0.23	0.19	0.18	0.14
28-May	—	—	—	—	0.6	0.64	0.69	0.22	0.26
29-May	—	—	—	—	0.34	0.34	0.33	NS	NS
30-May	—	—	—	—	0.12	0.17	0.24	NS	NS
2-June[c]	—	—	—	—	—	—	—	—	—
3-June	—	—	—	—	—	—	—	—	—
4-June	—	—	—	—	—	—	—	—	—
5-June	—	—	—	—	—	—	—	—	—
9-June[c]	—	—	—	—	—	—	—	—	—
10-June	—	—	—	—	—	—	0.05	—	0.06
11-June	NS	NS	—	—	0.06	0.06	0.06	0.06	0.06
12-June	0.05	0.05	—	—	—	0.04	0.06	0.06	0.06

a/ One samplecollected at the University of California, Davis campus, tested positive for methyl parathion. No samples collected at UC Davis tested positive for methyl paraoxon.

b/ A,B or A, B, C indicate co-located samplers at the collection sites.

c/ Dates when 3-hour samples were collected at Maxwell. Values listed represent the sum of values from three hour sample plus values from samples collected for the remainder of the day.

d/ "—" indicates sample concentration below the minimum detection level, of 0.02 ppt for methyl parathion and 0.05 ppt for methyl paraoxon respectively.

e/ "NS" indicates days when no samples were taken.

TABLE 15a. SUMMARY OF AMBIENT AIR CONCENTRATIONS OF METHYL PARATHION TOTAL RESIDUE (ng/m³).

County	Location	Total # of Samples	# of Sample Dates	# of Samples > MDL	Highest Daily Average Value[a] MP	Highest Daily Average Value[a] MP-oxon	Highest Daily Average Value[a] MP+MPEV	Average Values[a] MP	Average Values[a] MP-oxon	Average Values[a] MP+MPEV
Sutter	Trowbridge	44	15	10	1.1	0	0	0.8	0	0
	Robbins	37	12	10	0.7	0	0	0.1	0	0
Colusa	Maxwell	60	10	42	25.7	7.4	27.8	8.8	2.1	13
	Williams	36	11	25	21.8	1.2	22.6	4.3	0.9	6.7
Yolo	Davis	30	1	15	0.4	0	0	0	0	0

TABLE 15b. SUMMARY OF AMBIENT AIR CONCENTRATIONS OF METHYL PARATHION TOTAL RESIDUE (ppt).

County	Location	Total # of Samples	# of Sample Dates	# of Samples > MDL	Highest Daily Average Value[a] MP	Highest Daily Average Value[a] MP-oxon	Highest Daily Average Value[a] MP+MPEV	Average Values[a] MP	Average Values[a] MP-oxon	Average Values[a] MP+MPEV
Sutter	Trowbridge	44	15	10	0.1	0	0	0.07	0	0
	Robbins	37	12	10	0.07	0	0	0.01	0	0
Colusa	Maxwell	60	10	42	2.39	0.69	2.59	0.82	0.20	1.21
	Williams	36	11	25	2.08	0.11	2.10	0.40	0.08	0.62
Yolo	Davis	30	1	15	0.04	0	0	0	0	0

[a] Average of positive samples only.

5.2.5. Discussion

5.2.5.1. Methyl parathion

Methyl parathion concentrations measured at Trowbridge and Robbins varied insignificantly from background concentrations measured at Davis. These low concentrations in ambient air could be a result of the relatively low amount of methyl parathion applied in these areas or possible adverse meteorological conditions. Twenty-seven applications of methyl parathion were made to rice fields in townships adjacent to sampling sites at Trowbridge and Robbins. Average methyl parathion concentrations were 0.8 ng/m^3 (0.08 ppt) for Trowbridge and 0.5 ng/m^3 (0.05 ppt) for Robbins. Of interest is the methyl parathion detection on June 12 at Trowbridge, apparently corresponding with an application of 34 lbs of methyl parathion one mile from the sampler. Methyl parathion had not been applied to townships adjacent to Trowbridge since May 28, 1986. Methyl paraoxon was not detected in samples collected at Trowbridge, Robbins, or Davis.

In the Maxwell/Williams area, 236 applications of methyl parathion were made throughout May and June 1986 (Table 9). Ambient air concentrations of methyl parathion at Maxwell were relatively higher than those observed at Williams and measured concentrations may be related to the placement of the air samplers. Air samplers at Maxwell were placed less than 0.3 miles from rice fields where methyl parathion was being applied, while the air samplers at Williams, were placed within the city limits approximately one mile from the nearest rice fields. The application of 1,174 lbs of methyl parathion AI to 1,657 acres in the Maxwell/Williams area on May 13, 1986 was the second highest daily application for the month. This application coincided with the highest 24-hour concentration of methyl parathion of 25.7 ng/m^3 (2.39 ppt) detected in this study. The greatest application of methyl parathion to fields in Townships adjacent to Maxwell/Williams was 1,433 lbs AI to 3,082 acres on May 15, 1986. Methyl parathion and methyl paraoxon air concentrations in samples collected on May 15 were 13.7 ng/m^3 and 7.4 ng/m^3 (1.27 ppt and 0.69 ppt), respectively, for Maxwell and 5.6 ng/m^3 and 0.9 ng/m^3 (0.52 ppt and 0.08 ppt), respectively, for Williams. There were only six reported applications of methyl parathion during the first two weeks of June near Maxwell/Williams. Correspondingly, the ambient concentrations of methyl parathion during that period were very low (Table 10a).

The general lack of applications of methyl parathion in the Trowbridge/Robbins area compared to the Maxwell/Williams area may be explained by the following reasons. 1) DPR's recommendations for study locations and best times to monitor airborne levels were determined in 1985 based on the historical use of methyl parathion through 1984 whereas the monitoring was performed in 1986. Changes in agricultural practices could account for decreased methyl parathion applications in these areas in 1986. 2) The population of tadpole shrimp in rice fields, the main target organism, may not have reached the economic threshold level and therefore methyl parathion applications were not required. 3) Satisfactory control of tadpole shrimp populations may have been achieved via applications of other pesticides, reducing or eliminating the need for methyl parathion applications for that year. 4) Fewer fields were planted to rice.

Methyl parathion was applied near the sampling site at Maxwell on three (of 5) dates when 3-hour samples were collected. These dates were May 12 (70 lbs), May 19 (1,000 lbs), and June 2 (60 lbs). Methyl parathion was not applied in the Maxwell area on May 27, or June 9. Methyl parathion applications on May 19, corresponded with positive detections of both methyl parathion and methyl paraoxon in 3-hour samples. Non-detection of methyl parathion and methyl paraoxon on the other days when 3-hour samples were collected may be due the lower amounts of methyl parathion applied on those dates. Seiber *et al.* (1987), attribute the apparent correlation between the high air concentrations of methyl parathion and application of the pesticide, as well as the concomitant decrease in air concentrations following application to pesticide drift during application, rather than pesticide volatilization from treated rice-field water following application. The high concentrations of methyl parathion found in samples collected upwind, both during and after application, lend support to this hypothesis.

5.2.5.2. Methyl Paraoxon

Methyl paraoxon is created by oxidative conversion of methyl parathion in the presence of sunlight. This reaction may occur in the environment as well as within sample collection tubes exposed to sunlight. As part of their quality control procedures, the UCD researchers spiked field sample tubes with a known quantity of methyl parathion and analyzed the samples for both methyl parathion and methyl paraoxon. Upon analysis, they discovered a 48% conversion of methyl parathion to methyl paraoxon (16 sampling dates). The high conversion rate was attributed to the exposure of unprotected sample tubes to sunlight. The procedure was repeated twice under ambient conditions similar to those recorded during the study period and with proper shielding from sunlight, with results showing no significant conversion of methyl parathion to methyl paraoxon. All field samples were protected from sunlight during sampling and storage prior to analysis.

Overall, methyl paraoxon concentrations ranged from 3% to 71% of methyl parathion concentrations, averaging 24% at Maxwell, and 31% at Williams. The average methyl paraoxon concentration at Maxwell was 2.1 ng/m^3 (0.20 ppt) and the average concentration at Williams was 0.9 ng/m^3 (0.08 ppt). Based on the amounts reported above, the average methyl paraoxon concentrations were approximately 27% of methyl parathion concentrations. This suggests that when air concentrations of methyl parathion are low, concentrations of methyl paraoxon will be lower, and that when the airborne concentrations of methyl parathion are close to or below the MDL methyl paraoxon concentrations are expected to be undetectable.

The presence of methyl paraoxon in air has been attributed to the photo-oxidation of airborne methyl parathion rather than to the volatilization of methyl paraoxon from rice field water (Seiber *et al.*, 1989). Supporting evidence for this conclusion comes from the greater water solubility of methyl paraoxon leading to a lower rate of volatilization from rice field water than that of methyl parathion. Additionally, methyl paraoxon's rate of hydrolysis in rice field water is rapid enough to account for the decrease in solubilized methyl paraoxon. Thus, the conversion of methyl paraoxon to dimethyl phosphoric acid and p-nitrophenol in water proceeds at faster rates than reaction rates that govern volatilization from water into the atmosphere.

5.2.5.3. Total Residue

The maximum 24-hour methyl parathion as total residue of 27.8 ng/m^3 (2.59 ppt) (Table 15) observed at Maxwell on May 13 is lower than the maximum ambient air concentrations of most cases as reported in the literature (Table 8). Factors that may contribute to lower total residue concentrations in air are the relatively low application rates of methyl parathion in California (0.75 lbs AI/acre vs. 2.5 lbs AI/acre elsewhere), the season of methyl parathion application, differing agricultural practices, and the crops to which methyl parathion was applied. The movement toward using less toxic, more selective pesticides instead of methyl parathion, and using this broad-spectrum insecticide more selectively, may also contribute to lower airborne concentrations of methyl parathion in California air.

5.3. Air Monitoring of Methyl Parathion Associated with an Application

5.3.1. Abstract

Concentrations of methyl parathion in air were measured (ARB, 1989) immediately following an application of methyl parathion to a rice field. Duplicate air samples were collected at each sampling station, positioned at three locations around the field. One sampler was positioned 20 yards north of the treated field, another positioned 20 yards south of the treated field, and the third sampler located 250 yards south of the field. Samples were collected over 72 hours, five within the first 24 hours of sampling, and one for each of the two remaining 24-hour periods. The greatest concentration of methyl parathion, 512 ng/m^3 (47.62 ppt), was detected in samples (1.5 hour duration) collected immediately after application. These samplers were located 17 meters to the north (most often downwind) of the field. Concentrations steadily decreased over the sampling period with the final sample (48-72 hours post application) containing 29 ng/m^3 (2.7 ppt) of methyl parathion. Samples were not analyzed for methyl paraoxon.

Winds were light and variable for the first few hours of the study. Wind speed averaged 5.2 m/sec for the first 46 hours and generally blew from the south or southwest although winds blew west to east for several hours. Wind speed for the remaining 26 hours averaged 2.6 m/sec blowing from the northeast, north and northwest.

5.3.2. Introduction

On April 22, 1988, the ARB was requested to monitor airborne concentrations of methyl parathion associated with an application of the pesticide. A plan for monitoring a methyl parathion application was submitted to the department on May 18, 1988. Because monitoring was postponed until 1989, a second monitoring plan was submitted on May 3, 1989. A summary of their study follows.

5.3.3. *Materials and Methods*

The factors considered in choosing the site of the samplers were the cooperation of the grower, the location and accessibility of the rice field, and isolation of the chosen field from other fields being sprayed. Three sampler stations were set up with their specific locations determined by the prevailing wind patterns. One sampler was placed about 20 meters upwind from the field (or application site), and two samplers were placed downwind, approximately 20 and 225 meters from the field. The samplers were positioned in accordance with the criteria outlined in the USEPA Ambient Air Quality Monitoring, Data Reporting, and Surveillance Provisions, Title 40, CFR, section 58, Ambient Air Quality Surveillance, Appendix E, Probe Siting Criteria for Ambient Air Quality Monitoring. In addition, an on-site meteorological station was set up to measure wind direction and speed.

Each air sampler was fitted with duplicate cartridges containing XAD-2 resin adsorbent which were covered to protect the samples from sunlight. Each unit had a power supply, a pump, and a rotameter. Samples were collected at an approximate rate of 1.5 liters per minute. The air flow was recorded before and after the sampling period. Samples were stored on ice until reaching the ARB Northern Laboratory Branch and were kept frozen until analyzed according to the method described in Appendix 3. The samples were not analyzed for methyl paraoxon because a methyl paraoxon standard was not available.

An aerial application of methyl parathion, 1.0 lb AI/acre was made to a 80 acre rice field. Background samples were collected for one hour immediately prior to application. Samples of 1.2 to 1.5 hour duration were collected from the onset of application and for one hour following the end of the application. After this time, samples were collected only at the two sampling stations located approximately 20 meters from the field. Samples were collected approximately 1–3 hours, 3–7 hours, 7–18 hours, 18–24 hours, 24-48 hours, and 48–72 hours after application. Sampling durations were as follows: 1 hour for background concentrations; 1.5 hours during and immediately following the application; three hours, 11 hours, six hours, 24 hours, and 21 hours, consecutively; to 72 hours following the onset of application. Meteorological data for the first 24 hours of the study were obtained from the on-site station. Meteorological data for the second and third 24-hour sampling periods were obtained from a meteorological station, set up near the field. Wind data were used to determine the downwind and upwind directions for each sampling period.

5.3.4. *Results*

Methyl parathion results for application site air samples are presented in Table 16. Air concentrations of methyl parathion steadily decreased throughout the 72 hour sample period with the highest concentration 546 ng/m^3 (50.7 ppt) measured in the 1.5 hour sample collected immediately following sampling, in the most downwind sampler. The average concentration for this sampling period was 512 ng/m^3 (47.6 ppt). For samples collected from 1 to 3 hours and 3 to 7 hours post application, the wind predominantly blew from west to east and concentrations averaged 180 ng/m^3 (16.7 ppt) and 199 ng/m^3 (18.5 ppt) respectively. Methyl parathion concentrations from downwind samplers (Table 16) were 312 ng/m^3 (29.0 ppt), 70 ng/m^3 (6.5 ppt), 43 ng/m^3 (4.0 ppt), and 30 ng/m^3 (2.8 ppt) in samples collected from 7 to 18 hours, 18 to 25 hours, 25 to 49 hours, and 49 to 72 hours post application, respectively. Samplers were placed 18 meters from the treated field.

Throughout the sampling period, winds were variable. For the samples collected just prior to, during, and for seven hours after the application winds blew from the southwest or from the west at speeds less than 3.1 m/sec. Wind speed increased during the sample periods, 7–48 hours after application, blowing strongly from the south at speeds between 3.5 m/sec and 6.6 m/sec. In samples collected during this period, higher air concentrations of methyl parathion were measured in samples collected on the north side of the field. From 48 hours to the end of the study, the wind direction shifted, blowing from the north at approximately three meters per second.

TABLE 16.

AIR CONCENTRATIONS OF METHYL PARATHION FOLLOWING AN APPLICATION

Sample	Time after Application	Sampling Period (hr)	Sample Volume (m^3)	Average (n=2) Concentration (ng/m^3)	(ppt)
1N[a]	Background	1.2	0.11	–[b]	–
1S	Background	1.2	0.11	–	–
1S-2	Background	0.9	0.08	–	–
2N[c]	Application	1.5	0.14	512	47.62
2S	plus	1.4	0.12	219	20.37
2S-2	1 hour	1.2	0.11	–	–
3N	1 to 3 hr	1.6	0.14	161	14.97
3S		1.6	0.14	199	18.51
4N	3 to 7 hr	3.0	0.27	121	11.25
4S		3.0	0.27	277	25.76
5N[c]	7 to 18 hr	11.5	1.04	312	29.02
5S		11.6	1.04	99	9.21
6N[c]	18 to 25 hr	6.0	1.62	70	6.51
6S		6.0	1.62	34	–
7N[c]	25 to 49 hr	24.3	2.19	43	4.0
7S		24.3	2.19	–	–
8N	49 to 73 hr	21.1	1.9	28	2.6
8S[c]		21.5	1.94	30	2.79

a/ Sample numbers identify the sampling sequence. N is the sample site 20 yards (18 meters) north, S is the sample site 20 yards south, and S-2 is the" sample site 250 yards (227.5 meters) south of the treated field.

b/ "–" Indicates that the level is below the MDL 20 ng/m^3 (1.86 ppt). Background MDL was approximately 200 ng/m^3 (18.60 ppt)

c/ Indicates which samples were collected downwind of field. Methyl parathion was applied at a rate of 1.0 lb AI/acre to an 80 acre field.

5.3.5. *Discussion*

Off-site airborne concentrations of methyl parathion have been shown to vary considerably (ARB, 1989; Seiber and McChesney, 1987; Jackson and Lewis, 1976). Although application rates were identical (1.0 lbs AI/acre), and samples were collected immediately following application, concentrations ranged from 512 ng/m^3 (ARB 1989) to 7,800 ng/m^3 (Jackson and Lewis, 1976). Furthermore, concentrations measured by ARB (512 ng/m^3) were approximately half of those reported by Seiber and McChesney (1987), 1,060 ng/m^3 (Table 7). Variations in reported concentrations may be attributed to 1) study type, and 2) sampler placement. Jackson and Lewis (1976) were measuring the rate of off–gassing from treated fields with samplers placed within and one meter from field boundaries. Seiber *et al.* (1987) and ARB (1989) measured airborne concentrations 15 meters and 18 meters from field boundaries, respectively.

Wind direction may also affect detectable concentrations of methyl parathion. During the collection of sample 3, the wind blew from west to east. During the collection of sample 4, the wind blew west to east for the first 2 hours (of 3) shifting to south to north for the final hour. During the collection of sample 5, winds blew predominately from south to north (10.5 hours), and shifted to southeast to northwest for the remaining hour. Methyl parathion concentrations in both north and south samplers were lower in samples 3 and 4 when winds blew from west to east as compared to concentrations measured in samples 2 or 5 when winds were first SE--SW shifting to N–S respectively.

Airborne concentrations of methyl parathion reported in this study (ARB, 1989), concentrations reported by Seiber and McChesney (1987), and concentrations reported by Jackson and Lewis (1979), suggest that methyl parathion persists at low concentrations in the atmosphere from two to six days following application. Methyl parathion concentrations reported by the ARB (1989) from samples collected 18 to 72 hours after application are similar to concentrations reported over a similar time period by Seiber and McChesney (1987). These concentrations in turn, were approximately 10-fold lower than the values reported by Jackson and Lewis (1979) at three days after application.

5.3.6. *Quality Control*

The analytical laboratory carried out quality control procedures to determine the efficiency of the XAD–2 resin to trap methyl parathion, the effectiveness of the method, and the storage stability of the samples after 14 days in the freezer (Appendix 3).

The efficiency of the XAD–2 resin was determined by spiking the resin with known quantities of methyl parathion, drawing air through the resin for 24 hours at two liters/minute, and then analyzing the amount of methyl parathion extracted from the resin. Between 90% to 105% of the methyl parathion spiked on the resin was recovered.
The effectiveness of the extraction method was determined by spiking the resin with known quantities of methyl parathion and analyzing the amount extracted from the resin. Recovery of methyl parathion averaged 104% and 115% for two different concentrations (2 replicates).

The stability of the pesticide over time in storage was determined by analyzing samples which were spiked with known quantities of methyl parathion and stored in the freezer for 14 days. These samples were found to have between 97% to 102% of the amount placed on the resin.

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APPENDIX 1

EQUATIONS USED.

1. Conversion Factors for Air Levels (Volume/Volume Basis):

$$ng/m^3 = \frac{\text{ng (on XAD resin)}}{\dfrac{[\text{Flow rate (lpm)}] \times [\text{sampling period (min)}]}{1000\ L/m^3}}$$

$= \text{lpm} \times \text{min} \times m^3/10^3L$ sampled × the number of minutes sampled.

WHERE: lpm is the number of Liters of air sampled per minute

2. Conversion of methyl paraoxon to methyl parathion equivalents:

$$\frac{mg/m^3 \text{ methyl paraoxon} \times 263.2}{247.1} = mg/m^3 \text{ methyl parathion equivalent.}$$

WHERE: 263.2 is the molecular weight of methyl parathion and 247.1 is the molecular weight of methyl paraoxon.

3. Conversion of ng/m³ to ppt:

a) For Methyl Parathion:

$$ng/m^3 = \frac{ppt \times 263.2}{24.5}$$

WHERE: 263.2 is the molecular weight of methyl parathion and 24.5 is the volume in liters at 25 °C and 760 mm Hg (one atmosphere)

Therefore, $1\ ng/m^3 = 0.092$ ppt
and $1\ ppt = 10.73\ ng/m^3$

b) For Methyl Paraoxon.

$$ng/m^3 = \frac{ppt \times 247.1}{24.5}$$

WHERE: 247.1 is the molecular weight of methyl paraoxon and 24.5 is the volume in liters at 25 °C and 760 mm Hg (one atmosphere)

Therefore, $1\ ng/m^3 = 0.099$ ppt
and $1\ ppt = 10.10\ ng/m^3$

APPENDIX 2

LAB ANALYSIS

Extraction of Samples

The XAD-4 resin from high and low volume air samples was extracted in the following manner. For low volume samples, 90 ml of ethyl acetate was added to the resin in a 250 ml Erlenmeyer flask and then swirled for 30 minutes. The solvent was decanted and filtered through Whatman number one filter paper into a 500 ml sample storage container.

Fresh solvent (60 ml) was added to the flask and then swirled for 15 minutes. The solvent was then transferred and 50 ml of fresh solvent was added and the flask was swirled once more for 10 minutes. For high volume samples, the initial volume of ethyl acetate was 150 ml while successive aliquots were 100 ml. The size of the flask was 500 ml. Samples were concentrated on a steam bath using a Kuderna Danish apparatus to approximately 6 ml. Further reduction of solvent, if necessary, was accomplished using a 3-ball micro Snyder column and volumes adjusted for analysis.

Gas Chromatography

Methyl parathion and the oxon of methyl parathion were analyzed on a Hewlett Packard 5710A with a nitrogen-phosphorous detector. The column was a 30 m x 0.31 mm DB-5 WCOT fused silica megabore with 0.25 micron film thickness. Flow rates for air, helium, and hydrogen gases were 70, 6 and 5.5 ml/min, respectively. Temperatures for injector, column and detector were 250 °C, 210 °C, and 250 °C, respectively.

A Tracor MT-220 with a flame photometric detector and a phosphorous filter (526 nm) was also used for methyl parathion analysis when there was a question of interference or need of confirmation for those samples that approached the limit of detection. The column was a 6 ft. × 1.8 inch 3% OV-210 on 80–100 mesh Chrom W HP. Flow rates for nitrogen (carrier), air and hydrogen were 55 ml/min, 80 ml/min, and 60 ml/min, respectively.

Quality Assurance

A four or five point standard curve was made using a variable volume injection technique. Samples were then double injected and the average of the two areas used to calculate the concentration of methyl parathion. A standard was injected after every other sample and compared to the original standard curve. The analysis was considered valid if the standard agreed within three percent of the original standard curve. A recovery study (Table 1) was done before any samples were extracted and resin spikes and blanks were done once a week.

Minimum Detectable Limit

The minimum detectable limit (MDL) for methyl parathion was calculated to be 0.2 ng/m^3 (0.019 ppt) based on the following:
0.10 nanograms was detectable in a 6 ml injection from a total sample volume of 0.5 ml derived from an air sample of 50 m^3. The MDL for methyl paraoxon was 0.5 ng/m^3 (0.05 ppt).

Three-hour samples had MDL of 0.9 ng/m^3 for methyl parathion and 2.2 ng/m^3 for methyl paraoxon.

Table 1. Recovery Data for Spikes and Freezer Study

Chemical	Amount Spiked	Percent Recovered 1	2	3	Average % Recovered	Standard Deviation
Me Parathion	2.0 mg	90.6	97.9	104.2	97.6	6.8
Me Parathion	100 ng	106	110	118	111	6.1
Me Paraoxon	100 ng	81	111	68.1	86.7	22.0
Freezer Spikes						
Chemical						
Me Parathion	100 ng	86.4	81.7	90.1	86.1	4.2
Me Paraoxon	100 ng	59.3	68.3	72.1	66.5	6.6

APPENDIX 3

Method ADDL003
August 27, 1985
Revision: Prelim.

Draft 2

Approved : __________.
Page 1 of 8.

METHOD FOR THE DETERMINATION OF SELECTED ORGANOPHOSPHATE PESTICIDES IN AMBIENT AIR

1. Scope

This document describes a method for the sampling and analysis of parathion, methyl parathion, paraoxon, malathion, and diazinon at concentrations normally found in ambient air. This method was developed based on NIOSH, USEPA, and the California Department of Food and Agriculture published methods.

2. Summary of Method

After sampling using a low-volume system comprising pump, controller, glass fiber pre-filter, and purified XAD-2 absorbant trap, the exposed filter and absorbant are desorbed with 2.0 milliliters of 80/20 isooctane/acetone mixture. Two microliters of the extract are injected using splitless mode technique into a gas chromatographic system equipped with a 30 meter DB-5 capillary column, thermionic detector (TSD), and data system. The resultant peaks are identified by characteristic retention times and quantified in reference to external standards, The identity of a component may be confirmed by use of a column with different characteristics, a second detector system, or by GC/MS.

3. Interferences/Limitations

3.1 Components having similar GC retention times will interfere, causing misidentification and/or erroneous quantitation.

3.2 Extreme care must be taken to insure that sample losses do not occur due to leaks in the sampling system or to sample handling within the laboratory. All glassware must be thoroughly cleaned to insure that cross-contamination does not occur between samples. Samples are to be protected from sunlight during sampling and storage.

4. Apparatus

4.1 Varian Model 3300 Gas Chromatograph equipped with thermionic detector (TSD and a vista 402 Data System.

4.2 DB-5 fused silica capillary column, 30 meters by 0.32 mm i.d., 1 mm film thickness.

4.3 Amber vials, 3.7 ml capacity, with Teflon-lined septum caps.

4.4 Sample agitator with timer and sample rack.

4.5 Microliter syringes, 5-50 ml sizes.

4.6 Low-volume sampler pump and flow controller capable of maintaining preset flow rates of 6 lpm over a 24 hour period. Sampling system must have an accurate timer system to control sampling interval and to indicate total sampling elapsed time.

4.7 Sampling head capable of containing a 37 mm glass fiber filter in-line with a 6" x 1/4" absorption tube containing XAD-2 absorbant.

4.8 Glass fiber filters, 37 mm diameter, type A/E, with Teflon holder.

4.9 Glass absorption tubes, 6" x 1/4", containing purified XAD-2 absorbant; 400 mg primary section, 200 mg secondary section. Absorbant must be demonstrated to be free of interfering substances by analysis of unused absorbants (analytical blanks).

5. Reagents

5.1 80/20 iso-octane/acetone desorbant solvent: Mix 80 ml pesticide grade iso-octane (trimethyl pentane) and 20 ml pesticide grade acetone in a clean glass bottle equipped with Teflon-lined screw cap. CAUTION: Flammable - DO NOT expose to heat or oxidizers.

5.2 Stock Standards: Individual 1000 mg/ml certified stock standards containing diazinon, parathion, methyl parathion, paraoxon may be obtained from Nanogens, Inc. CAUTION: Toxic - Use protective gloves in handling these materials.

5.3 Working Standards: Dilute 20 ml of each stock standard into 50/50 iso-octane/acetone solvent and dilute to 10.0 ml. This corresponds to a 2.0 mg/ml standard.

6. Instrument Conditions

Column: 30m x 0.32 mm i.d. DB-5 fused silica capillary column;

Temperature	Injector:	250° C
	Detector:	350° C
	Oven:	50° C, initial, hold for 1 minute, ramp at 5° C/min to 140 °C; ramp at 4° C/min to 260° C, 4 minute hold;
Flow Rates:	Helium	50 cc/min at splitter, 0.5 min splitless hold. Carrier velocity after splitter opens: 25 cm/sec.
	Hydrogen	4.5 cc/min
	Air	180.0 cc/min
Detector:	TSC	Range 11, Attenuation x 32,
Heater:		3.4 amp.

7. *Sample Collection*

7.1 Sampling flow controllers and indicators must be calibrated by trained personnel before the unit can be placed in the field. The flow rate calibration must be verified monthly at the flow rate used for sampling.

7.2 The 37 mm glass fiber filter and holder, as received from the laboratory, is placed in the sampling head compartment. The compartment is then assemble, taking care that the unit is completely sealed. The filter holder may be handled, but care must be taken not to touch or contaminate the filter itself. If any question of contamination is present, the filter is discarded and a new filter is installed.

7.3 The sealed XAD-2 absorbant tube is prepared for use by snapping off the sealed ends with the tool provided. The open tool is then placed in the sampling train using 1/4" polyethylene tubing fittings, making sure that the flow indicator arrow printed on the tube fittings points in the direction of the flow. The tube fittings must be tightened sufficiently to insure that the system is leak free.

7.4 After starting the pump system, the flow must be adjusted to approximately 6 lpm. The time, indicated flow, and true flow rates (read from the calibration graph) must be recorded. The filter and absorbant trap numbers must be recorded. The elapsed time meter is reset to zero. The system is leak-checked by sealing the sampler inlet and insuring that the flow rate is zero.

7.5 After a 24 hour sampling period, the indicated flow and true flow rates must be recorded. The sampler system is deactivated, the elapsed time and actual time is recorded, and the filter and absorbant tube removed. The filter and cassette holder is placed into a plastic shipping container. The tube is sealed using the red end-caps provided. The filter and tube are immediately sent to the laboratory with all sampling information and chain of custody.

8. *Instrument Calibration Procedure*

8.1 Before a standard solution may be injected, a system blank must be analyzed. This is done by injecting 2.0 ml of 80/20 iso-octane/ acetone solvent for analysis. If the subsequent analysis indicates interferences or contamination, the solvent must be replaced.

8.2 A method blank must be analyzed for every 10 samples. This is done by randomly selecting a "blank" (unused) filter and absorbant tube, desorbing (extracting) the "blank" filter and absorbant, and injecting 2.0 ml of the resultant extract into the instrument for analysis. If interferences or contamination is noted, the source must be found, and if possible, eliminated.

8.3 Instrument calibration is performed by injection of 2.0 ml of a 2.0 mg/ml mixed standard. The resultant chromatogram and calculated concentrations must be inspected to insure proper integration and consistency with previous analyses. The data is then used to calibrate the method. The instrument data system will not accept updated response factors which are not within 10 percent of historic data.

8.4 If the analyses are to be made daily, a weekly analysis of three standards (2.0, 0.4, and 0.08 mg/ml) must be made to insure that the method exhibits linear response. In addition a weekly "spiked" sample of 0.8 micrograms per absorbant tube of individual pesticides must be taken through the entire analytical scheme to insure that the method is in control. The results of these analyses must be entered on the method control charts.

9. Analysis of Samples.

9.1 After removal of the glass fiber filter from the Teflon filter holder using stainless steel forceps, the filter is carefully rolled and placed in a 3.7 ml vial. The filter must be forced into the bottom of the vial to insure that the entire filter is in contact with the solvent.

9.2 After removal of the red end-caps from the absorbant tube, the tube is scored using a glass cutter above the location of the retainer spring. Using the tool provided, the tube is then broken and the retainer spring removed. The glass wool plug and the primary (400 mg) section of XAD-2 is placed in a 3.7 ml vial. Similarly, the secondary section (200 mg) of XAD-2 in placed in a second vial. Make sure all vials are properly identified.

9.3 Place 2.0 ml desorbing solvent (80/20) into vials, cap tightly and place on vial agitator for 45 minutes.

9.4 After desorption, 2.0 ml of each extract is injected into the chromatographic system for analysis. the data generated from the glass fiber filter extract is recorded as "filterable". The combined results are recorded as total.

9.5 The results are recorded in micrograms/m³ and are calculated as follows:

$$\text{mg/m}^3 = \frac{\text{mg/ml (found} \times 2 \times 1000}{\text{average flow (lpm)} \times \text{time sampled (minutes).}}$$

10. Method Sensitivity, Precision, and Accuracy.

10.1 The method sensitivity, precision, and accuracy are outlined in Table I. The data were generated using standards.

11. Desorption Efficiencies and Sample Stability.

11.1 The primary section of the XAD-2 sampling tubes was "spiked" with 10 ml of solutions containing known amounts of the five organophosphate pesticides of interest. The tubes were then sealed, placed in a refrigerator for storage, and tested after intervals to test the stability of the materials on the sorbant. Table II presents the results of this study. Note that the samples are stable over a period of two weeks.

11.2 The primary section of the XAD-2 sampling tube was "spiked" with 10 ml of solutions containing known amounts of the five pesticides of interest. The "spiked" tubes were then placed in the low volume sampling device and sampled at a flow rate of 7.5 lpm for differing lengths of time. Both the primary and secondary sections of the sampling tubes were desorbed and analyzed. The results are presented in Table III. Note that at the sampling rate of 7.5 lpm, the breakthrough volume of all pesticides tested is greater than 14 m^3.

Table I

Compound	Conc. 1 mg/ml	S.D.* %	Conc. 2 mg/ml	S.D. %	Conc. 3 mg/ml	S.D. %	MDL mg/ml
Diazinon	2.0	11.6	0.4	14	0.08	7	0.04
Methyl Parathion	2.0	2.3	0.4	8	0.08	7	0.02
Paroxon	2.0	11.0	0.4	12	0.08	11	0.04
Malathion	2.0	9.6	0.4	10	0.08	8	0.04
Parathion	2.0	8.3	0.4	8	0.08	9	0.02

Compound	Correlation Coefficient	Slope	Intercept (mg/ml)
Diazinon	0.998	0.980	0.031
Methyl Parathion	0.998	0.988	0.016
Paroxon	0.997	0.996	0.026
Malathion	0.997	0.991	0.032
Parathion	0.998	1.003	-0.015

* S.D. = Relative Standard Deviation

Table II
ORGANO-PHOSPHATE PESTICIDE STABILITY STUDY

Storage Time, Hrs	0	24	48	96	192	384
Compound	Amount Recovered, µg (Percent)					
Diazinon	1.68 (98)	1.60 (93)	1.70 (99)	1.58 (92)	1.64 (95)	1.62 (94)
Methyl Parathion	1.45 (83)	1.42 (84)	1.50 (86)	1.40 (82)	1.42 (82)	1.35 (78)
Paroxon	1.42 (97)	1.40 (96)	1.48 (101)	1.38 (94)	1.40 (96)	1.41 (96)
Malathion	1.42 (91)	1.38 (88)	1.50 (96)	1.40 (90)	1.42 (91)	1.48 (95)
Parathion	1.50 (88)	1.52 (89)	1.60 (94)	1.46 (86)	1.50 (88)	1.42 (84)

Table III
ORGANOPHOSPHATE PESTICIDE SAMPLING AND BREAKTHROUGH STUDY

Volume Sampled (7.5 lpm), m^3	3.6	7.2	10.8	14
Compound	Amount Recovered, µg (percent) Primary/µg (percent) Secondary			
Diazinon	1.60 (93)/0 (0)	1.66 (96)/0 (0)	1.56 (91)/0 (0)	1.92(100)/0 (0)
Methyl Parathion	1.47 (84)/0 (0)	1.55 (89)/0 (0)	1.44 (83)/0 (0)	1.62 (93)/0 (0)
Paroxon	1.40 (96)/0 (0)	1.48(101)/0 (0)	1.38 (94)/0 (0)	1.50(103)/0 (0)
Malathion	1.44 (93)/0 (0)	1.48 (95)/0 (0)	1.40 (90)/0 (0)	1.50 (96)/0 (0)
Parathion	1.52 (89)/0 (0)	1.56 (92)/0 (0)	1.42 (84)/0 (0)	1.56 (92)/0 (0)